

U.S. Patent Application Serial No. 09/926,838
Amendment dated October 8, 2003
Reply to OA of July 8, 2003

REMARKS

Claims 1-27 are pending in this application. Claims 1, 9 and 15 have been amended herein. The amendments to the claims are discussed below with reference to the claim objections and rejections.

Claims 1 and 9 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. (Office action paragraph no. 1)

(a) The Examiner refers to the linking group in La-Ld of claims 1 and 9 as being vague, and that the group listed as " C^O C" should be " $C\equiv C$ ". The Examiner is correct; the error was due to a computer font typographical error in the Preliminary Amendment. Claims 1 and 9 have been amended to correct this error.

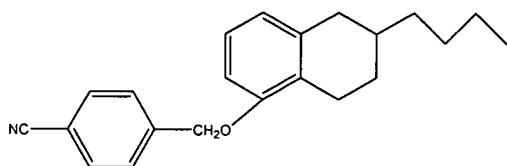
(b) The Examiner states that "the ring C being a phenylene in the provisos is vague because the ring C is tetrahydronaphthalene", noting that notation "C" should be ring -- E -- in claim 1. The Examiner is correct and the rejection is overcome by the amendment of claim 1. In the Amendment, the phrase "ring C and ring D are 1,4-phenylene" has been amended to --ring E and ring D are 1,4-phenylene" in three locations in claim 1.

Claims 1, 2, 5, 6, 8-12, 14, 16-18 and 21-24 are rejected under 35 U.S.C. 102(b) as being anticipated by JP 06-279321. (Office action paragraph no. 3)

Applicants have obtained and attached an English translation of JP06-279321 for the convenience of the Examiner.

The rejection of claims 1, 3-4, 7, 8, 12, 14, 16-18 and 21-24 is overcome by the amendment to claim 1 inserting – , OCH₂ – between “Lc and Ld are single bonds” and “or -COO linkages” in the fourth paragraph from the end of the claim. The rejection of claims 9-11 is respectfully traversed.

With regard to the rejection of claims 1, 3-4, 7, 8, 12, 14, 16-18 and 21-24, the Examiner refers in particular to Example 5 on page 13 of the reference, which is



. The Examiner apparently considers this to correspond to

the case in claim 1 where Z is a cyano group, $n^c = 0$, $n^d = 1$, R is an unsubstituted and saturated alkyl group, $n^a = n^b = 0$, and Lc is OCH₂.

With the amendment, the fourth paragraph from the end of claim 1 now reads:

“in a case in which Z is a cyano group, R is an unsubstituted and saturated alkyl group or alkoxyl group, $n^a = n^b = n^c = 0$ and $n^d = 1$, or $n^a = n^b = n^d = 0$ and $n^c = 1$, ring E and ring D are 1,4-phenylene groups, Lc and Ld are single bonds, -OCH₂- or -COO- linkages, and ring C is said general formula (IIa), then at least one of X¹, X² and X³ represents a fluorine atom;”.

That is, Example 5 of the reference meets the requirements for Z, R, n^a , n^b , n^c , n^d , Lc, Ld, and C in this proviso, but does not have a fluorine atom at position corresponding to X¹, X² or X³.

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Therefore, Example 5 of the reference does not meet the limitations of claim 1, as amended.

The rejection of claims 9-11 is respectfully traversed, as Applicants submit that formula 5 of the reference does not anticipate claims 9-11, even without the amendment to claim 1. Anticipation would require that $Lc = OCH_2$. In claims 9-11, La, Lb, Lc and Ld are limited and cannot be OCH_2 .

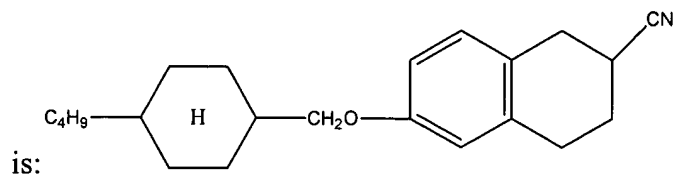
Applicants therefore submit that claims 1, 2, 5, 6, 8-12, 14, 16-18 and 21-24 are not anticipated by JP 06-279321, and reconsideration of the rejection is respectfully requested.

Claims 1, 3-4, 7-12, 14, 16-18 and 21-24 are rejected under 35 U.S.C. 102(b) as being anticipated by JP 06-256284. (Office action paragraph no. 4)

Applicants have obtained and attached an English translation of JP06-256284 for the convenience of the Examiner.

The rejection is respectfully traversed.

The Examiner cites in particular Example 5 on page 13 or 15. This compound



. Here, "H" presumably means a cyclohexane

ring. The Examiner apparently considers this to meet the limitations of claim 1 when $Z = CN$, $n^c = n^d = 0$, and n^a or $n^b = 1$, with the other equal to 0, and La or Lb equal to CH_2O .

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However, Applicants note that the last paragraph of claim 1 reads:

“and in a case in which ring C is said general formula (IIb), at least one of n^c and n^d is 1”.

Example 5 of the reference corresponds to a case where ring C is formula (IIb), which according to the present claims would require “at least one of n^c and n^d is 1”. That is, ring D or ring E must be present in this case according to the claims, but there is no corresponding ring in Example 5 of the reference.

In addition, Applicants further note that Example 5 of the reference cannot anticipate claims 9-11, since Example 5 corresponds to a case where La or Lb is CH_2O .

Applicants therefore submit that claims 1, 3-4, 7-12, 14, 16-18 and 21-24 are not anticipated by JP 06-256284, and reconsideration of the rejection is respectfully requested.

Claims 1, 2, 4, 7-14, 16-18 and 21-24 are rejected under 35 U.S.C. 102(a)/(b) as being anticipated by US 6,491,989 or WO 99/23047. (Office action paragraph no. 5)

Applicants note that Manero et al. U.S. 6,491,989 has a 371 date of July 10, 2000 (effective U.S. filing date), and was patented on December 10, 2002. Since the present application is based on international application PCT/JP99/04919, filed on September 10, 1999, Manero et al. '989 is not itself a reference under 35 U.S.C. 102(a), (b), or (e).

WO99/23047 was published on May 14, 1999, and therefore WO'047 is a reference under 35 U.S.C. 102(a), but **not** 102(b). Since WO'047 is published in German, Applicants here refer to Manero et al. '989 **only** as a translation of reference WO'047.

The rejection of claims 1, 2, 4, 7-14, 16-18 and 21-24 is respectfully traversed.

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The Examiner refers in particular to compounds Ii-Ij and Is-It in columns 42 and 43. The Examiner apparently considers these to correspond to the case where Z = fluorine, and $n^c=n^d=0$.

However, Applicants note that compounds Ii-Ij and Is-It of Manero would correspond to ring C of the present invention being (IIa), X^2 being F, and X^1 being R^{11} , where R^{11} is a straight-chain or branched alkyl or alkoxy chain having 1 to 20 or 1 to 19 carbon atoms, in which one or two hydrogen atoms may be replaced by F (see column 43, lines 40 to 43). However, in the present application, X^1 , X^2 , X^3 , X^4 , X^5 and X^6 must be hydrogen atoms or fluorine atoms. Compounds Ii-Ij and Is-It are therefore inconsistent with present claim 1.

Applicants therefore submit that the pending claims are not anticipated by WO99/23047, and reconsideration of the rejection is respectfully requested.

Claims 25-27 are rejected under 35 U.S.C. 103(a) as being unpatentable over JP 06-279321, JP 06-256284, US 6,491,989 or WO 99/23047. (Office action paragraph no. 7)

The rejection of claims 25-27 is overcome by the amendment to claim 1.

Claims 25-27 depend ultimately on independent claim 1 or independent claim 15. Claim 15 was indicated as allowable if amended into independent form, and claim 15 has been so amended. Applicants have amended claim 1 to overcome the rejection over JP 06-279321, and have traversed the rejection of claim 1 as anticipated by JP 06-256284 or WO 99/23047.

Applicants submit that claim 1 is also non-obvious over the cited references, taken individually or in combination, since none of the references suggests the recited chemical structural limitations of the claim. Applicants therefore submit that claims 25-27 are novel and non-obvious

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over the cited references.

Claim 15 is objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. (Office action paragraph no. 8)

Claim 15 has been amended to be in independent form, incorporating the limitations of claim 1.


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If, for any reason, it is felt that this application is not now in condition for allowance, the Examiner is requested to contact Applicants undersigned agent at the telephone number indicated below to arrange for an interview to expedite the disposition of this case.

In the event that this paper is not timely filed, Applicants respectfully petition for an appropriate extension of time. Please charge any fees for such an extension of time and any other fees which may be due with respect to this paper, to Deposit Account No. 01-2340.

Respectfully submitted,

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PATENT TRADEMARK OFFICE

Enclosures: Partial translation of JP 06-279321 and JP 06-256284
Full JPO machine translation of JP 06-279321 and JP 06-256284

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Japanese Patent Application, First Publication No. Hei 6-279321

Int.Cl.⁵: C07C 13/48, 23/18, 25/18, 41/09, 43/20

Application No.: Japanese Patent Application No. 5-41516

Filing Date: March 2, 1993

Applicant: Takeda Chemical Industries, Ltd.

Applicant: Hitachi, Ltd.

Inventors: Mitsuru KAWATA et al.

Representative: Attorney, Akira UCHIDA et al.

[Title of the Invention]

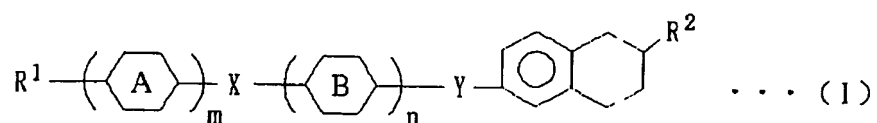
2-ALKYL-6-SUBSTITUTED-1,2,3,4-TETRAHYDRONAPHTHALENE

DERIVATIVE, PROCESS FOR PRODUCING THE SAME, AND LIQUID CRYSTAL
COMPOSITION CONTAINING SAID DERIVATIVE

[Claims]

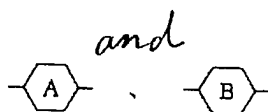
[Claim 1] A 2-alkyl-6-substituted-1,2,3,4-tetrahydronaphthalene derivative represented by the following general formula (I):

[Chemical Formula 1]



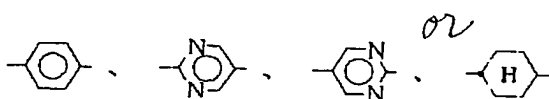
[wherein R¹ represents (1) an optionally substituted alkyl group having 1 to 14 carbon atoms, an alkoxy group, or an acyloxy group, (2) a halogen atom, or (3) a cyano group; R² represents an optionally substituted alkyl group having 1 to 14 carbon atoms;

[Chemical Formula 2]



may be the same or different and each represents

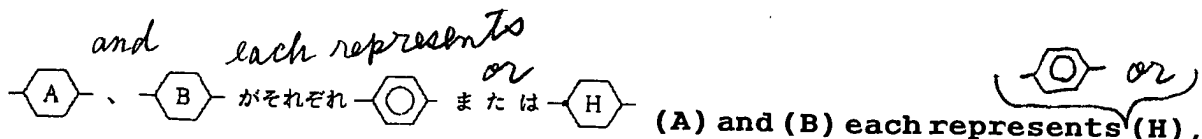
[Chemical Formula 3]



which may be substituted; X and Y each represents a single bond, a (thio)ester bond, a methyleneoxy bond, or an oxymethylene bond; and m and n each represents 0, 1 or 2 and are not simultaneously 0, provided that at least one of X and Y represents a single bond when n is 0].

[Claim 2] The compound according to claim 1, wherein, in the general formula (I), R^1 is a straight-chain alkyl group having 3 to 8 carbon atoms, R^2 is a straight-chain alkyl group having smaller carbon atoms than those of R^1 ,

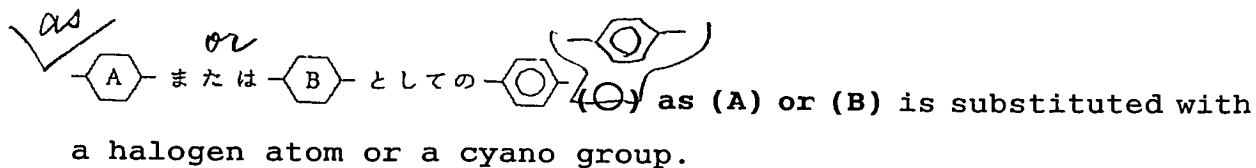
[Chemical Formula 4]



X and Y each represents a carboxylate ester bond or a methyleneoxy bond.

[Claim 3] The compound according to claim 2, wherein

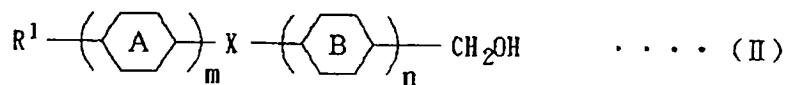
[Chemical Formula 5]



[Claim 4] The compound according to claim 3, wherein the halogen atom is a fluorine atom.

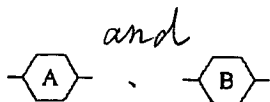
[Claim 5] A process for producing the compound according to claim 1, which comprises subjecting an alcohol component compound, as a skeleton component, represented by the following general formula (II):

[Chemical Formula 6]



[wherein R^1 , X, m, n and

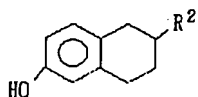
[Chemical Formula 7]



are as defined in claim 1] or an active derivative thereof and a phenolic compound represented by the following general formula

(III):

[Chemical Formula 8]

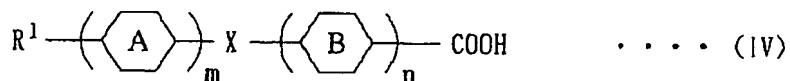


... (III)

[R² is as defined in claim 1] to the condensation reaction.

[Claim 6] A process for producing the compound according to claim 1, which comprises subjecting a carboxylic acid compound, as a skeleton component, represented by the following general formula (IV):

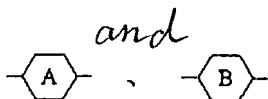
[Chemical Formula 9]



... (IV)

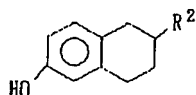
[wherein R¹, X, m, n and

[Chemical Formula 10]



are as defined in claim 1] or an active derivative thereof and a phenolic compound represented by the following general formula (V):

[Chemical Formula 11]



.... (V)

[R² is as defined in claim 1] to the condensation reaction.

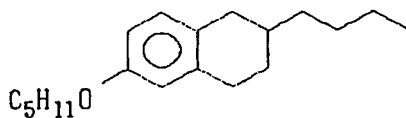
[Claim 7] A liquid crystal composition comprising at least one kind of the compound according to claim 1.

[0019]

[Examples] The present invention will be described in detail by way of examples, but is not limited thereto.

Reference Example 1

[Chemical Formula 29]



100 ml of a solution of 0.11 mol of LDA (lithium diisopropylamide) in tetrahydrofuran was ice-cooled and 17.6 g (0.10 mol) of 6-methoxy-1-tetralone was added. After stirring for 20 minutes, 60 ml of a solution of 67.5 g (0.50 mol) of crotyl bromide in HMPA (triamide hexamethylphosphate) was added dropwise.

After the completion of dropwise addition, the temperature was returned to room temperature, followed by stirring for 2 hours. The reaction solution was poured into water and extracted with ether and, after concentrating the ether layer, the residue was purified by silica gel chromatography (eluent: ethyl acetate/hexane = 5/95) to obtain 11.8 g of 6-methoxy-2-butenyl-1-tetralone. Under ice cooling, 16.0 g (0.12 mol) of anhydrous aluminum chloride was dissolved in 150 ml of dry ether and 4.56 g (0.12 mol) of aluminum lithium hydride was added, followed by stirring for 10 minutes. 6.90 g (0.03 mol) of ketone obtained above was gently added. After returning to room temperature and stirring for 30 minutes, the reaction solution was carefully poured into dilute hydrochloric acid and separated. After concentrating the ether layer, the residue was purified by silica gel chromatography (eluent: ethyl acetate/hexane = 2/98) to obtain 6.60 g of 6-butenyl-2-methoxy-5,6,7,8-tetrahydronaphthalene. 6.40 g (0.0296 mol) of the resulting tetrahydronaphthalene was dissolved in 60 ml of methanol and 0.5 g of 5% palladium-carbon was added, and then the catalytic hydrogen reduction was conducted at normal temperature under normal pressure. The catalyst was removed by filtration and the filtrate was concentrated to obtain 6.57 g of 6-butyl-2-methoxy-5,6,7,8-tetrahydronaphthalene. 6.50 g (0.0298 mol) of the resulting methoxy compound was dissolved in 120 ml of acetic acid and 20 ml of 47% hydrobromic acid was added,

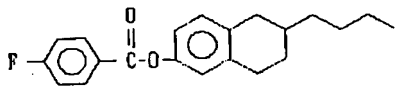
and then the mixture was heated under reflux overnight. After the reaction solution was concentrated, the residue was poured into water and extracted with ether. The ether layer was concentrated and then sufficiently dried to obtain 5.90 g of 6-butyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene. 0.5 g (2.45 mmol) of the resulting hydroxy compound and 1.85 g (12.3 mmol) of n-amy bromide were added to 15 ml of dimethyl sulfoxide and 0.12 g (2.94 mmol) of 60% sodium hydride was added in several portions, followed by stirring at 70°C for 30 minutes. The reaction solution was poured into water and extracted with ether and, after concentrating the ether layer, the residue was purified by silica gel chromatography (eluent: ethyl acetate/hexane = 2/98) to obtain 0.22 g (32.8%) of the desired product.

¹H-NMR (200MHz, CDCl₃)

δ: 6.93 (d, 1H), 6.65 (dd, 1H), 6.59 (brs, 1H), 3.88 (t, 2H), 2.84-2.63 (m, 2H), 2.47-2.23 (m, 1H), 1.96-0.79 (m, 22H)

[0020] Example 1

[Chemical Formula 30]



After 0.5 g (2.45 mmol) of the hydroxy compound obtained in Reference Example 1 was dissolved in 15 ml of dichloromethane,

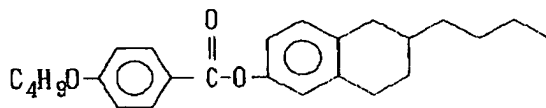
1.24 g (12.3 mmol) of triethylamine was added and 0.47 g (2.94 mmol) of p-fluorobenzoyl chloride was added in several portions, followed by stirring at room temperature for one hour. After adding a small amount of dilute hydrochloric acid, the reaction solution was extracted with dichloromethane. The organic layer was concentrated and the residue was purified by silica gel chromatography (eluent: ethyl acetate/hexane = 10/90) to obtain 0.63 g (78.8%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 8.20 (m, 1H), 7.27-7.04 (m, 2H), 6.91 (m, 1H), 2.93-2.62 (m, 2H), 2.56-2.27 (m, 1H), 2.01-1.08 (m, 13H), 1.01-0.70 (m, 3H)

[0021] Example 2

[Chemical Formula 31]



To 0.8 g (4.12 mmol) of p-(n-butoxy)-benzoic acid, 3 ml of thionyl chloride was added and the mixture was heated under reflux at 80°C for 2 hours while stirring. After the completion of the reaction, toluene was added and the reaction solution was concentrated under reduced pressure. To 15 ml of tetrahydrofuran, 0.5 g (2.45 mmol) of the hydroxy compound obtained in Reference Example 1 and 1.24 g (12.3 mmol) of triethylamine were added, and

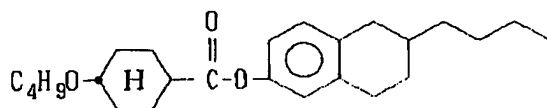
then acid chloride obtained above was added dropwise in several portions. After the completion of dropwise addition and stirring at 80°C for 2 hours, the reaction solution was concentrate and the residue was purified by silica gel chromatography (eluent: chloroform) to obtain 0.52 g (55.8%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 8.13 (d, 2H), 7.08 (d, 1H), 7.03-6.86 (m, 4H), 4.03 (t, 2H),
2.94-2.67 (m, 2H), 2.54-2.27 (m, 1H), 1.98-1.14 (m, 14H),
1.12-0.83 (m, 6H)

[0022] Example 3

[Chemical Formula 32]



To 0.68 g (3.69 mmol) of trans-4-n-cyclohexanecarboxylic acid, 3 ml of thionyl chloride was added and the mixture was heated under reflux at 80°C for 2 hours while stirring. After the completion of the reaction, toluene was added and the reaction solution was concentrated under reduced pressure. To 15 ml of tetrahydrofuran, 0.5 g (2.45 mmol) of the hydroxy compound obtained in Reference Example 1 and 1.24 g (12.3 mmol) of triethylamine were added and acid chloride obtained above was added dropwise in several portions. After the completion of dropwise addition,

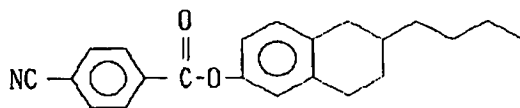
the mixture was stirred at 80°C for 2 hours. After the completion of the reaction, the precipitate was removed by filtration and the filtrate was concentrated, and then the residue was purified by silica gel chromatography (eluent: chloroform) to obtain 0.53 g (58.4%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 7.02 (d, 1H), 6.76 (m, 2H), 2.88-2.63 (m, 3H), 2.52-2.27 (m, 2H), 2.18-2.03 (m, 2H), 1.98-0.72 (m, 28H)

[0023] Example 4

[Chemical Formula 33]



To 20 ml of THF, 0.5 g (2.45 mmol) of the hydroxy compound obtained in Reference Example 1 and 1.24 g (12.3 mmol) of triethylamine were added and 0.61 g of p-cyanobenzoyl chloride was added in several portions. While stirring at 80°C for 1.5 hours, the mixture was heated under reflux. The precipitate was removed from the reaction solution by filtration and a small amount of dilute hydrochloric acid was added to the filtrate, followed by extraction with dichloromethane. After the organic layer was concentrated, the residue was purified by silica gel chromatography (eluent: chloroform) and then recrystallized from hexane to obtain

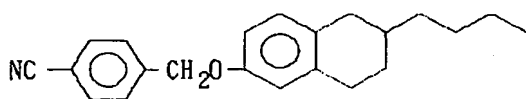
0.5 g (61.2%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 8.29(d, 2H), 7.82(d, 2H), 7.12(d, 1H), 6.93(m, 2H),
2.95-2.79(m, 3H), 2.48-2.31(m, 1H), 2.03-1.22(m, 9H),
0.98-0.87(m, 3H)

[0024] Example 5

[Chemical Formula 34]



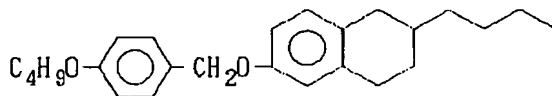
To 20 ml of dimethyl sulfoxide, 0.5 g (2.45 mmol) of the hydroxy compound obtained in Reference Example 1 and 2.4 g (12.3 mmol) of α -bromo-p-trinitrile were dissolved and 0.12 g (2.94 mmol) of 60% sodium hydride was added in several portions, followed by stirring at 70°C for 1.5 hours. The reaction solution was concentrated and the residue was purified by silica gel chromatography (eluent: ethyl acetate/hexane = 25/75) to obtain 0.23 g (29.4%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 7.67(d, 2H), 7.54(d, 2H), 6.98(d, 1H), 6.70(m, 2H), 5.08(s, 2H),
2.89-2.54(m, 3H), 2.51-2.22(m, 1H), 2.09-0.72(m, 12H)

[0025] Example 6

[Chemical Formula 35]



0.5 g (2.45 mmol) of the hydroxy compound obtained in Reference Example 1, 2.21 g (12.3 mmol) of *n*-butoxybenzyl alcohol and 0.96 g (3.68 mmol) of triphenyl phosphine were dissolved in 20 ml of dichloromethane and 0.64 g (3.68 mmol) of diethyl azodicarboxylate was added dropwise while stirring, followed by stirring at room temperature overnight. The reaction solution was concentrated and the residue was purified by silica gel chromatography (eluent: ethyl acetate/hexane = 10/90) to obtain 0.26 g (29.0%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 7.33(d, 2H), 6.96(d, 1H), 6.88(d, 2H), 6.73(m, 2H),
4.94(s, 2H), 3.97(t, 2H), 2.86-2.63(m, 2H), 2.47-2.22(m, 1H),
1.97-1.13(m, 14H), 1.08-0.78(m, 6H)

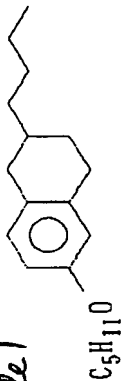
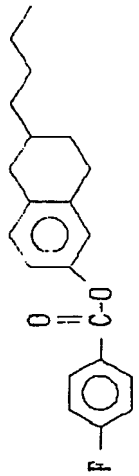
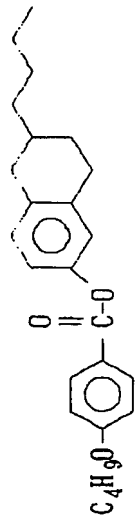
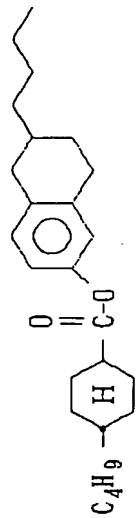
[0026] Measurement of physical properties

The measurement of the phase transition temperature of the compounds obtained in the above Reference Examples and Examples and identification of the phase were conducted by visual observation using a polarization microscope and a differential scanning calorimeter (DSC). Δn and $\Delta \epsilon$ were measured according to the method described in the document. The results are shown

Table 1

Example 例 Structural formula 構造式 表 1 transition temperature 相転移温度 (°C) Δn $\Delta \epsilon$

Table 1

Reference Example 1 参考例 1		oil	—	—	—
Example 1 実施例 1		\rightleftharpoons N — I >-30 21.5	0.081	0.35	
Example 2 実施例 2		$K \rightleftharpoons$ N — I 38.0 89.6	0.076	(0.003)	
Example 3 実施例 3		$K \rightleftharpoons$ N — I 14.0 60.5	0.051	微小 very small	

Examples**Structural formula****Phase transition temperature****Reference Example 1****Example 1****Example 2****Example 3****very small****[0028]****[Table 2]**

Table 1 (continued)

表 - I (つづき)

Example 4 実施例 4		$\begin{array}{c} 88.2 \\ \text{K} \rightleftharpoons \text{N} \text{---} \text{I} \\ 106.0 \quad 128.9 \end{array}$	0.120	4.21 (-10°C) 4.98 (-30°C)
Example 5 実施例 5		$\begin{array}{c} \text{K} \text{---} \text{N} \text{---} \text{I} \\ 43 - 52 \end{array}$		
Example 6 実施例 6		$\begin{array}{c} \text{K} \xrightarrow{26.9} \text{N} \xrightarrow{26.9} \text{I} \\ 26.9 \quad 26.9 \end{array}$	0.07	

(注) 液晶相などの各相は、次の記号で示した。

I : 等方相 ; N : ネマチック相 ; K : 結晶相

(Note) Abbreviations of various phases such as liquid crystal phase are as follows:

I: isotropic phase, N: nematic phase, and
K: crystal phase

Table 1 (continued)

Example 4

Example 5

Example 6

(Note) Abbreviations of various phases such as liquid crystal phase are as follows:

I: isotropic phase, N: nematic phase, and K: crystal phase.

[0029]

[Effects of the Invention]

2-alkyl-6-substituted-1,2,3,4-tetrahydronaphthalene derivative, which is a compound of the present invention, is a novel compound and is also a component which is useful in the production of a liquid crystal composition used in a liquid crystal flat panel display. That is, this compound is physically and chemically stable and stably exhibits preferable liquid crystal phase (nematic liquid crystal phase). Also the compound is excellent in compatibility with other various liquid crystal compounds such as esters, ethers, carbonyls, biphenyls, phenylcyclohexanes and heterocyclic type liquid crystal compounds and can increase an N-I point and improve the other physical properties by adding to these compounds or its liquid crystal composition. In the construction of the liquid crystal composition used in the liquid crystal flat panel display, the present invention provides a compound which is useful as a component.

Japanese Patent Application, First Publication No. Hei 6-256284

Int.Cl.⁵: C07C 255/47, 253/30, 327/24, 327/26, C07D 239/26

Application No.: Japanese Patent Application No. 5-41517

Filing Date: March 2, 1993

Applicant: Takeda Chemical Industries, Ltd.

Applicant: Hitachi, Ltd.

Inventors: Mitsuru KAWATA et al.

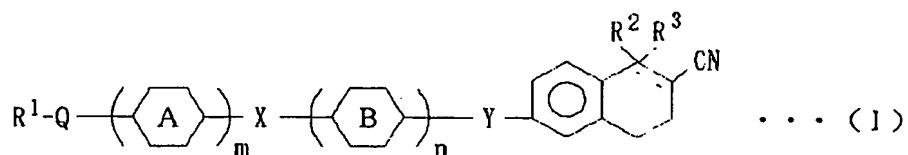
Representative: Attorney, Akira UCHIDA et al.

[Title of the Invention] 2-CYANO-6-SUBSTITUTED-3,4-DIHYDRO (OR 1,2,3,4-TETRAHYDRO)NAPHTHALENE DERIVATIVE AND LIQUID CRYSTAL COMPOSITION CONTAINING SAID DERIVATIVE

[Claims]

[Claim 1] A 2-cyano-6-substituted-3,4-dihydro (or 1,2,3,4-tetrahydro)naphthalene derivative represented by the following general formula (I):

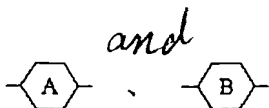
[Chemical Formula 1]



[wherein R^1 represents an optionally substituted alkyl group having 1 to 14 carbon atoms; R^2 and R^3 each independently or simultaneously represents a hydrogen atom or a halogen atom, or R^2 and R^3 are combined to form =O; Q represents a single bond, an ether bond,

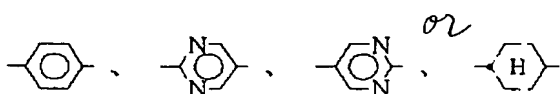
or an ester bond,

[Chemical Formula 2]



may be the same or different and represent

[Chemical Formula 3]



which may be substituted; X and Y each represents a single bond, a (thio)ester bond, a methyleneoxy bond, or an oxymethylene bond;

[Chemical Formula 4]

represents a single bond or a double bond; and m and n each represents 0, 1, or 2 and are not simultaneously 0, provided that at least one of Q and X represents a single bond when m is 0, and at least one of X and Y represents a single bond when n is 0].

[Claim 2] The compound according to claim 1, wherein, in the general formula (I), R^1 is a straight-chain alkyl group having 3 to 6 carbon atoms, R^2 and R^3 each independently or simultaneously represents a hydrogen atom or a fluorine atom, or R^2 and R^3 are combined to form =O, Q is a single bond,

[Chemical Formula 5]

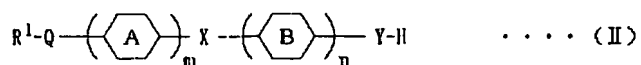
and each represents

 (A) and (B) each represents (H), X and Y each represents a carboxylate ester bond or a methyleneoxy bond, and at least one of m and n is 1 and the other one is 0.

[Claim 3] The compound according to claim 1, wherein the halogen atom is a fluorine atom.

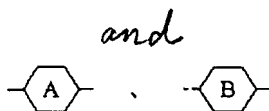
[Claim 4] A process for producing the compound according to claim 1, which comprises subjecting a skeleton component compound represented by the following general formula (II):

[Chemical Formula 6]



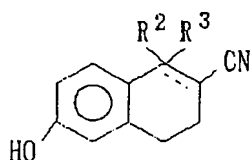
[wherein R^1 , X, Y, m, n and

[Chemical Formula 7]



are as defined in claim 1] or an active derivative thereof and a phenolic compound represented by the following general formula (III):

[Chemical Formula 8]

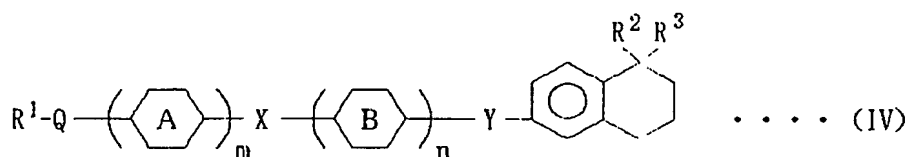


. (III)

[R² and R³ are as defined above] to the condensation reaction.

[Claim 5] A process for producing the compound according to claim 1, which comprises reacting a tetralone derivative represented by the following general formula (IV):

[Chemical Formula 9]



[wherein R¹, R², R³, Q, X, Y, A, B, m and n are as defined in claim 1.] with hydroxylamine and ethyl formate or sodium ethoxide.

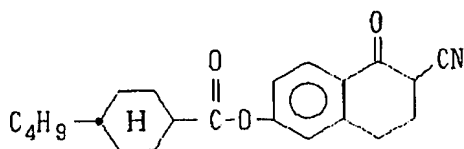
[Claim 6] A liquid crystal composition comprising at least one kind of the compound according to claim 1.

[0020]

[Examples] The present invention will be described in detail by way of examples, but is not limited thereto.

Example 1

[Chemical Formula 32]



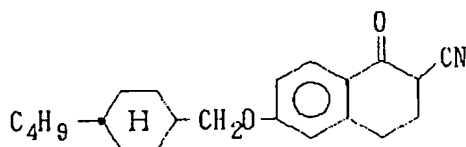
According to Production Example (A), the synthesis was conducted. First, 8.0 g (0.0398 mol) of 2-cyano-6-methoxy-1-tetralone (2) synthesized by a known method described in the document [Synthesis, 449, (1981)] was dissolved in 150 ml of dimethylformamide and 5.0 g (0.0713 mol) of sodium thiomethoxide was added, followed by stirring at 140°C for 10 hours. The reaction solution was gently poured into cold dilute hydrochloric acid and extracted with ether. The ether layer was concentrated and sufficiently dried to obtain 7.0 g of 2-cyano-6-hydroxy-1-tetralone (3). 3.74 g (0.02 mol) of the resulting phenolic compound and 10.12 g (0.1 mol) of triethylamine were dissolved in 50 ml of methylene chloride and 4.04 g (0.02 mol) of acid chloride of trans-4-butyl-cyclohexanecarboxylic acid was added, followed by stirring at room temperature for one hour. The reaction solution was concentrated and the residue was purified by silica gel chromatography (eluent: chloroform) to obtain 2.60 g of the desired product.

¹H-NMR (200MHz, CDCl₃)

δ: 8.10(d, 1H), 7.10-7.00(m, 2H), 3.75(dd, 1H), 3.20-3.00(m, 2H), 2.65-2.35(m, 3H), 2.20-2.05(m, 2H), 2.00-1.80(m, 2H), 1.70-0.80(m, 14H)

[0021] Example 2

[Chemical Formula 33]



According to Production Example (B), the synthesis was conducted. First, 25.0 g (0.142 mol) of 6-methoxy-1-tetralone was dissolved in 500 ml of acetic acid and 80 ml of 47% hydrobromic acid was added, and then the mixture was heated under reflux overnight. After the reaction solution was concentrated, the residue was poured into water and extracted with ether. The ether layer was concentrated and the residue was recrystallized from chloroform to obtain 17.50 g (76.1%) of 6-hydroxy-1-tetralone (4). 4.86 g (0.03 mol) of the resulting phenolic compound, 5.73 g (0.033 mol) of trans-4-butylcyclohexyl methanol and 11.79 g (0.045 mol) of triphenyl phosphine were dissolved in 90 ml of tetrahydrofuran and 7.83 g (0.045 mol) of diethyl azodicarboxylate was added dropwise, followed by stirring at room temperature for 3 hours. The reaction solution was concentrated and the residue was purified by silica gel chromatography (eluent: ethyl acetate/hexane = 7/93) to obtain 8.20 g (87.0%) of 6-(trans-4-butylcyclohexyl)-methoxy-1-tetralone. In the very same manner as in aforementioned method [Synthesis, 449, (1981)], 4.70 g (63.0%) of the desired product was obtained from 6.90 g

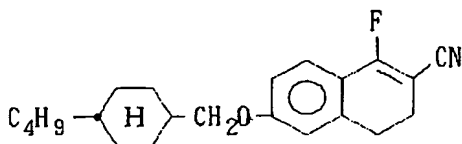
(0.022 mol) of the resulting tetralone.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 8.00(d, 1H), 6.85(dd, 1H), 6.70(brs, 1H), 3.85(d, 2H), 3.70(dd, 1H),
3.20-2.90(m, 2H), 2.60-2.30(m, 2H), 2.00-0.80(m, 19H)

[0022] Example 3

[Chemical Formula 34]



To 10 ml of THF cooled to -15°C to -20°C using ice-ethanol, 1 ml (7.4 mmol) of dimethylaminosulfur trifluoride was added, and then a solution prepared by two drops of concentrated sulfuric acid and 0.5 g (1.48 mmol) of the ketone compound obtained in Example 2 in 15 ml of tetrahydrofuran was added dropwise. After the completion of dropwise addition, the mixture was stirred at 70°C for 2 hours. After the completion of the reaction, the reaction solution was poured into water and an aqueous sodium hydrogencarbonate solution was added. After extracting with ethyl acetate, the organic layer was concentrated and the residue was purified twice by silica gel chromatography (first eluent: chloroform, second eluent: ethyl acetate/hexane = 5/95) to obtain 0.24 g (47.7%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 7.42(d, 1H), 6.81-6.74(dd, 1H), 6.71(brs, 1H), 3.76(d, 2H),

2.87(t,2H), 2.66-2.53(m,2H), 1.93-0.80(m,19H)

Elemental analysis:

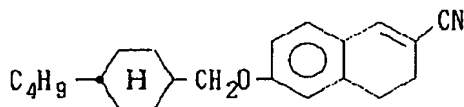
Molecular formula (M.W.): $C_{22}H_{28}NOF$ (341.46886)

Element	Calculated	Measured
C	77.38	77.23
H	8.26	8.25
N	4.10	4.27
F	5.56	5.59
O	4.69	-

[0023]

Example 4

[Chemical Formula 35]



1.00 g (2.95 mmol) of the ketone compound obtained in Example 2 was dissolved in 40 ml of 2-propanol and 1.13 g (30 mmol) of sodium borohydride was added under ice cooling, followed by returning to room temperature and further stirring for 3 hours. The reaction solution was poured into dilute HCl and extracted with ethyl acetate, and then the organic layer was concentrated and the residue was purified by silica gel chromatography (eluent: chloroform) to obtain 1.10 g of a higher alcohol prepared by reduction. The resulting alcohol was dissolved in 50 ml of toluene and 5 g of potassium hydrogensulfate was added, and then the mixture was heated under reflux at 120°C for 3 hours. The inorganic matter

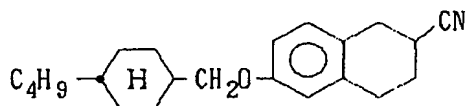
was removed by filtration and the filtrate was concentrated, and then the residue was purified by silica gel chromatography (eluent: chloroform) to obtain 0.87 g (91.3%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 7.15(s, 1H), 7.05(d, 2H), 6.75-6.65(m, 2H), 3.75(d, 2H), 2.85(t, 2H), 2.50(t, 2H), 2.00-0.80(m, 19H)

[0024] Example 5

[Chemical Formula 36]



0.48 g (1.5 mmol) of the dihydronaphthalene derivative obtained in Example 4 was dissolved in 30 ml of methanol and 2.2 g (90 mmol) of magnesium was added under ice cooling, followed by stirring at room temperature for 3 hours. After magnesium was dissolved by adding dilute hydrochloric acid to the reaction solution, extraction was conducted by adding ether. The ether layer was concentrated and the residue was purified by silica gel chromatography (eluent: chloroform) to obtain 0.48 g (98.5%) of the desired product.

$^1\text{H-NMR}$ (200MHz, CDCl_3)

δ : 6.95(d, 1H), 6.75-6.55(m, 2H), 3.70(d, 2H), 3.15-2.70(m, 4H), 2.30-0.80(m, 22H)

[0025] Measurement of physical properties

The measurement of the phase transition temperature of the compounds obtained in the above Examples and identification of the phase were conducted by visual observation using a polarization microscope and a differential scanning calorimetry (DSC). Δn and Δe were measured according to the method described in the document. The results are shown in Table 1.

[0026]

[Table 1]

Table 1
 表 - 1 transition temperature
 phase 相 転移温度 (°C)
 Example 実施例
 Structural formula 構造式

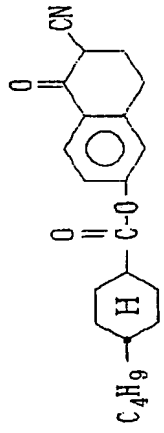
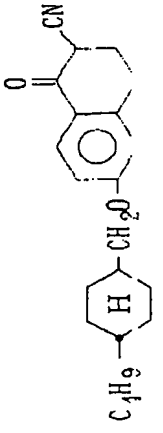
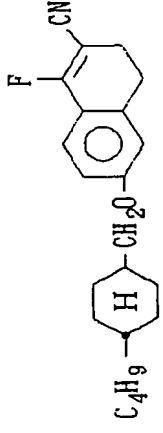
Example 実施例	Structural formula 構造式	phase 相 転移温度 (°C)	Δn	$\Delta \epsilon$
1		$\begin{array}{c} 84.1 \quad 96.1 \\ \leftarrow \text{N} \rightarrow \\ \text{K} \xrightarrow{120.0} \text{I} \end{array}$	0.045	-
2		$\begin{array}{c} 62.0 \\ \leftarrow \text{S}_A \rightarrow \\ \text{K} \xrightarrow{86.2} \text{I} \end{array}$	-	-
3		$\begin{array}{c} 49.3 \quad 69.1 \\ \leftarrow \text{N} \rightarrow \\ \text{K} \xrightarrow{73.4} \text{I} \end{array}$	0.12	14.6

Table-1

Examples

Structural formula

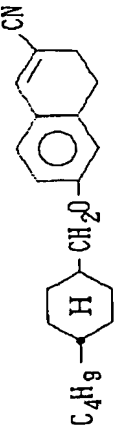
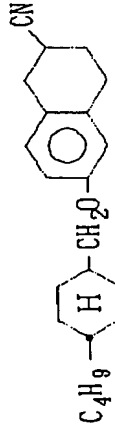
Phase transition temperature

[0027]

[Table 2]

Table 1 (continued)

表 - 1 (つづき)

4		$\begin{array}{c} \text{K} \rightleftharpoons \text{N} \xrightarrow{\quad} \text{I} \\ 58.8 \quad 84.9 \end{array}$	0.15	10.36 (30.5°C)
5		$\begin{array}{c} \swarrow \quad \text{N} \xleftarrow{\quad} \text{I} \\ \text{K} \xrightarrow{\quad} \quad \quad 56.5 \end{array}$	0.072 (31°C)	3.31 (30°C)

(注) 液晶相などの各相は、次の記号で示した。

I : 等方相 ; N : ネマチック相 ; S_A : スメクチック A 相 ; K : 結晶相

(Note) Abbreviations of various phases such as

liquid crystal phase are as follows:

I : isotropic phase, N : nematic phase,

S_A : smectic A phase, and K : crystal phase

Table-1 (continued)

(Note) Abbreviations of various phases such as liquid crystal phase are as follows:

I: isotropic phase, N: nematic phase, S_A: smectic A phase, and K: crystal phase.

[0028]

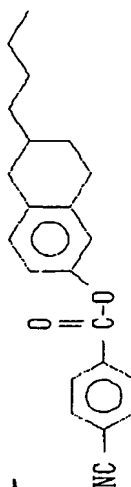
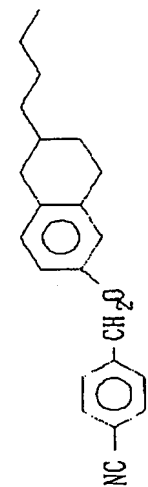
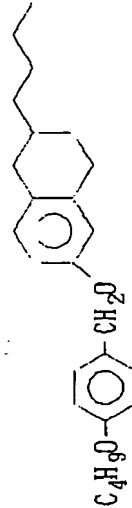
[Effects of the Invention]

2-alkyl-6-substituted-1,2,3,4-tetrahydronaphthalene derivative, which is a compound of the present invention, is a novel compound and is also a component which is useful in the production of a liquid crystal composition used in a liquid crystal flat panel display. The compound of the present invention is characterized in that it has high physical and chemical stability and exhibits a stable nematic phase, and also includes a compound having large dielectric anisotropy ($\Delta\epsilon$). Therefore, the compound of the present invention is an additive, which is effective to lower a voltage of a liquid crystal composition, with respect to threshold voltage and saturation voltage required to drive a liquid crystal display, and it is provided as a useful component in the construction of a practical liquid crystal composition. The compound of the present invention is excellent in compatibility with other various liquid crystal compounds such as ester, ether, carbonyl, biphenyl, phenylcyclohexane and heterocyclic type liquid crystal compounds and can increase an N-I point and improve the other physical properties by adding to a liquid crystal composition containing these liquid crystal compounds. In the construction

of the liquid crystal composition used in the liquid crystal flat panel display, the present invention provides a compound, which is useful as a component, and also provides a practical liquid crystal composition containing at least one kind of the compound.

Table 1 (continued)

表 - I (つづき)

Example 4 実施例 4		$\begin{array}{c} 88.2 \\ K \rightleftharpoons N \text{ --- } I \\ 106.0 \quad 128.9 \end{array}$	0.120	4.21 (-10°C) 4.98 (-30°C)
Example 5 実施例 5		$\begin{array}{c} K \text{ --- } N \text{ --- } I \\ 43 - 52 \end{array}$		
Example 6 実施例 6		$\begin{array}{c} K \xrightarrow{26.9} N \xrightarrow{26.9} I \\ \swarrow \quad \searrow \end{array}$	0.07	

(注) 液晶相などの各相は、次の記号で示した。

I : 等方相 ; N : ネマチック相 ; K : 結晶相

(Note) Abbreviations of various phases such as liquid crystal phase are as follows:
 I: isotropic phase, N: nematic phase, and
 K: crystal phase

Table 1 (continued)

Example 4

Example 5

Example 6

(Note) Abbreviations of various phases such as liquid crystal phase are as follows:

I: isotropic phase, N: nematic phase, and K: crystal phase.

[0029]

[Effects of the Invention]

2-alkyl-6-substituted-1,2,3,4-tetrahydronaphthalene derivative, which is a compound of the present invention, is a novel compound and is also a component which is useful in the production of a liquid crystal composition used in a liquid crystal flat panel display. That is, this compound is physically and chemically stable and stably exhibits preferable liquid crystal phase (nematic liquid crystal phase). Also the compound is excellent in compatibility with other various liquid crystal compounds such as esters, ethers, carbonyls, biphenyls, phenylcyclohexanes and heterocyclic type liquid crystal compounds and can increase an N-I point and improve the other physical properties by adding to these compounds or its liquid crystal composition. In the construction of the liquid crystal composition used in the liquid crystal flat panel display, the present invention provides a compound which is useful as a component.

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

Bibliography.

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- (12) [Official Gazette Type] Open patent official report (A)
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- (43) [Date of Publication] October 4, Heisei 6 (1994).
- (54) [Title of the Invention] 2-alkyl-6-substitution - Liquid crystal constituent containing 1, 2, 3, 4-tetrahydronaphthalene derivatives, those manufacturing methods, and this derivative.
- (51) [The 5th edition of International Patent Classification]

C07C 13/48

23/18

25/18

41/09

43/20

D 7419-4H.

67/08

69/75

A 9279-4H.

Z 9279-4H.

69/92

69/94

253/30

255/50

255/54

255/55

327/26

7106-4H.

C07D239/36

8615-4C.

C09K 19/32

9279-4H.

19/34

9279-4H.

[Request for Examination] Un-asking.

[The number of claims] 7.

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* NOTICES *

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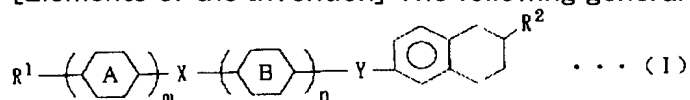
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Summary.

(57) [Abstract]

[Objects of the Invention] While it is chemically [physically] stable and a stable nematic phase is shown, offer a liquid crystal compound with a small refractive-index anisotropy (deltan).

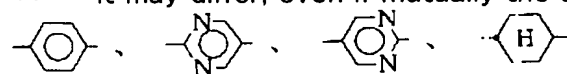
[Elements of the Invention] The following general formula (I), [Formula 1]



R1 shows among a formula [alkyl group [of the carbon numbers 1-14 by which (1) substitution may be carried out], alkoxy-group or acyloxy machine, (2) halogen atom, or (3) cyano group, and R2 shows the alkyl group of the carbon numbers 1-14 which may be replaced. [Formula 2]



** -- it may differ, even if mutually the same, and it may be replaced, respectively [Formula 3]



*****, and X and Y shall show single bond, ester (thio) combination, methylene oxy-combination, or oxy-methylene combination, respectively, m and n shall show 0, 1, and 2, respectively, and both shall not be 0 simultaneously. However, when n is 0, even if there are little X and Y either, one side shows single bond.] 2-alkyl-6-substitution come out of and expressed - 1, 2, 3, 4-tetrahydronaphthalene derivatives, those manufacturing methods, and liquid crystal constituent.

[Translation done.]

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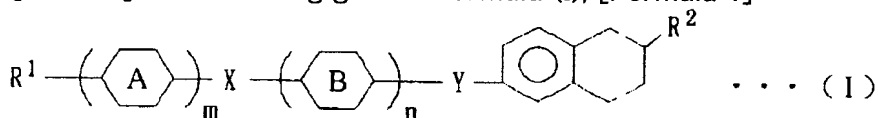
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CLAIMS

[Claim(s)]

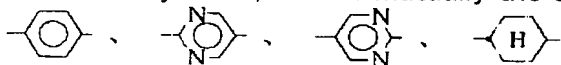
[Claim 1] The following general formula (I), [Formula 1]



R1 shows among a formula [alkyl group [of the carbon numbers 1-14 by which (1) substitution may be carried out], alkoxy-group or acyloxy machine, (2) halogen atom, or (3) cyano group, and R2 shows the alkyl group of the carbon numbers 1-14 which may be replaced. [Formula 2]

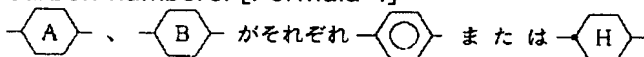


** -- it may differ, even if mutually the same, and it may be replaced, respectively [Formula 3]



*****, and X and Y shall show single bond, ester (thio) combination, methylene oxy-combination, or oxy-methylene combination, respectively, m and n shall show 0, 1, and 2, respectively, and both shall not be 0 simultaneously. However, when n is 0, even if there are little X and Y either, one side shows single bond.] 2-alkyl-6-substitution come out of and expressed - 1, 2, 3, 4-tetrahydronaphthalene derivative.

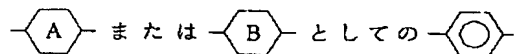
[Claim 2] The inside of a general formula (I), and R1 A carbon number is the alkyl group of 3-8 in the shape of a straight chain, and it is R2. R1 It is a straight chain-like alkyl group with few carbon numbers. [Formula 4]



The compound according to claim 1 X and whose Y come out, it is and are carboxylate combination or methylene oxy-combination, respectively.

[Claim 3]

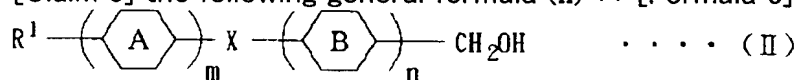
[Formula 5]



The compound according to claim 2 replaced by the ** halogen atom or the cyano group.

[Claim 4] The compound according to claim 3 whose halogen atom is a fluorine atom.

[Claim 5] the following general formula (II) ** [Formula 6]



the inside of [formula, R1, and X, m and n -- and . [Formula 7]

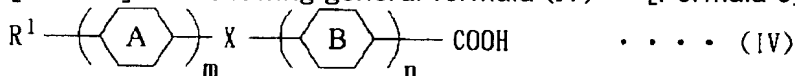


The alcoholic component compound or its activity derivative, and the following general formula (III) as a frame component expressed with] which has ***** 1 publication and this meaning [Formula 8]



It is the manufacture method of the compound according to claim 1 characterized by giving the phenol nature compound expressed with [R2 has claim 1 publication and this meaning] to a condensation reaction.

[Claim 6] the following general formula (IV) ** [Formula 9]



the inside of [formula, R1, and X, m and n -- and . [Formula 10]



The carboxylic-acid compound or its activity derivative, and the following general formula (V) as a frame component expressed with] which has ***** 1 publication and this meaning [Formula 11]



It is the manufacture method of the compound according to claim 1 characterized by giving the phenol nature compound expressed with [R2 has claim 1 publication and this meaning] to a condensation reaction.

[Claim 7] The liquid crystal constituent which contains at least one sort of a compound according to claim 1, and is characterized by the bird clapper.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

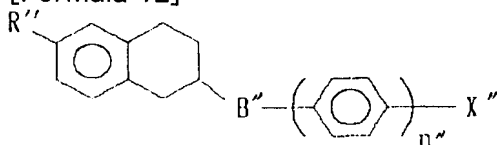
[0001]

[Industrial Application] this invention relates to the liquid crystal constituent which shows a liquid crystal phase and contains at least one sort of new liquid crystal compounds and them of low viscosity.

[0002]

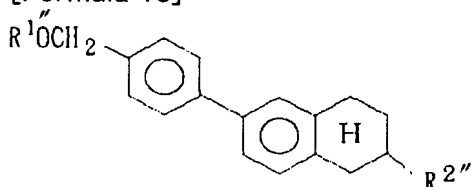
[Description of the Prior Art] A liquid crystal compound shows a dielectric constant anisotropy and an optical anisotropy with a liquid crystal phase. The application product which there are a nematic-liquid-crystal phase, a smectic-liquid-crystal phase, and cholesteric-liquid-crystal equality in a liquid crystal phase, among these used the nematic-liquid-crystal phase is put in practical use most widely. That is, the application product using these properties is developed by sign display rows including modulated light glass to flat-panel displays, such as a calculator, a clock, and a word processor, etc., it is various with progress of the latest electronics field, and the development is remarkable. the difference in a method which makes a liquid crystal compound drive -- a dynamic scattering type (DS type) -- it is twisted and is classified into a super-[a nematic type (TN type) and] torsion nematic type (STN type), a guest-host type (GH type), etc. Stability [as opposed to / naturally / physicochemical stability especially heat, light, moisture, air, etc. in the liquid crystal material used for these] is required. Moreover, liquid crystal material shows a desired liquid crystal phase by the broad temperature requirement including a room temperature as it can do, and it must be satisfied [with practical use level] of physical properties according to the purpose, such as operating voltage and responsibility. That is, in order for threshold voltage and a saturation voltage required for making a liquid crystal display element drive generally to carry out a thing low if possible and a speed of response early, the method of a low has the as much as possible good viscosity of liquid crystal material. 2 proposed from the former; 6-JI substitution naphthalene or 2, 6-JI substitution - 1, 2, 3, and 4-tetrahydronaphthalene compound (JP,61-282345,A, 62-444 each number official report) general formula is a useful material in case a lower formula prepares the constituent for nematic liquid crystal display elements. That is, there are some which show nematic nature with an item, and it is useful as expansion of the nematic temperature region of liquid crystal mixture, or an additive for the improvement of delta epsilon and delta n.

[Formula 12]



R'': It is a contrast improvement agent by low-battery drive to the alkyl or alkoxy-group pan of the alkyl of carbon numbers 1-10 or alkoxy-group B'':-CO-O- or -O-CO-X'':F, Cl or Br, or carbon numbers 1-10. The following nematic-liquid-crystal material, 2, 6-JI substitution - 1, 2, 3, and 4-tetrahydronaphthalene system compound (JP,60-209539,A and a general formula are a lower formula) is also known.

[Formula 13]



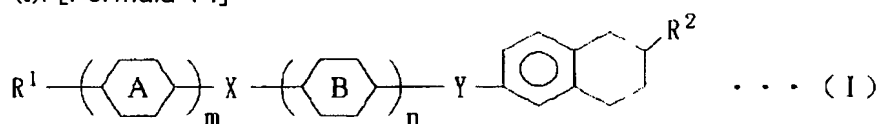
(Alkyl group of the R1 "R2'':carbon numbers 1-10)

[0003]

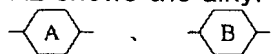
[Problem(s) to be Solved by the Invention] However, it is impossible to fill many above-mentioned physical properties with an item compound, and the present condition is having mixed several sorts of liquid crystal compounds, and the non-liquid crystal compound, and having gained practical demand characteristics. It is very important to develop the item compound which has many best possible physical properties in building the liquid crystal constituent to which these practical demand characteristics is satisfied. In case the purpose of this invention develops such a practical liquid crystal constituent, it is offering a useful new liquid crystal compound.

[0004]

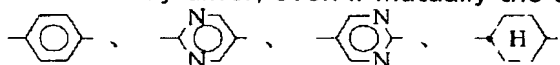
[Means for Solving the Problem] The summary of this invention is the following general formula (I). [Formula 14]



R1 shows among a formula [alkyl group [of the carbon numbers 1-14 by which (1) substitution may be carried out], alkoxy-group or acyloxy machine, (2) halogen atom, or (3) cyano group, and R2 shows the alkyl group of the carbon numbers 1-14 which may be replaced. [Formula 15]

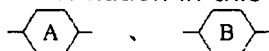


** -- it may differ, even if mutually the same, and it may be replaced, respectively [Formula 16]

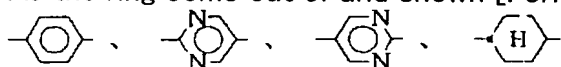


*****, and X and Y shall show single bond, ester (thio) combination, methylene oxy-combination, or oxy-methylene combination, respectively, m and n shall show 0, 1, and 2, respectively, and both shall not be 0 simultaneously. However, when n is 0, even if there are little X and Y either, one side shows single bond.] 2-alkyl-6-substitution come out of and expressed - It is in 1, 2, 3, and 4-tetrahydronaphthalene derivative, and the liquid crystal constituent containing the manufacture method of the above-mentioned compound and one or more sorts of above-mentioned compounds is included.

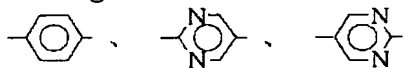
[0005] It sets to the compound expressed with the aforementioned general formula (I) concerning this invention, and is R1. And R2 It may differ, even if the same, and the alkyl group of carbon numbers 1-14 is shown, respectively. These alkyl groups may be any of a straight chain or branching. specifically For example, a methyl, ethyl, a propyl, butyl, a pentyl, a hexyl, a heptyl, In straight chain-like alkyl group rows, such as an octyl, a nonyl, a desyl, a undecyl, a dodecyl, tridecyl, and tetradecyl, an isopropyl, An isobutyl, sec-butyl, tert-butyl, an isopentyl, neopentyl, The alkyl group of letters of branching, such as a tert-pentyl, an iso hexyl, 1-methyl pentyl, 2-methyl pentyl, 5-methyl hexyl, 2 and 3, a 5-trimethyl hexyl, 2 and 7, a 8-trimethyl desyl, and a 4-ethyl-5-methyl nonyl, can be mentioned. R1 The alkoxy group of the carbon numbers 1-14 by which (1) substitution besides the above may be carried out or an acyloxy machine, (2) halogen atom, or (3) cyano groups are shown. R1 If it attaches, the alkyl group of 3-8, for example, a propyl, butyl, a pentyl, a hexyl, a heptyl, and an octyl have a desirable carbon number especially at the shape of a straight chain. On the other hand, about R2, it is R1. C1-6, such as the low-grade alkyl group of the shape of a straight chain with few carbon numbers, for example, a methyl, ethyl, a propyl, and a butyl An alkyl group etc. is desirable. Although single bond, ester (thio) combination, methylene oxy-combination, or oxy-methylene combination is included about the combination in a frame shown by X and Y, respectively, single bond and carboxylate combination are desirable especially. Any are sufficient although there are order ester combination and reverse ester combination as mentioned above also about the carboxylate combination in this case. Further, [Formula 17]



As the ring come out of and shown [Formula 18]



although ** is mentioned -- desirable [Formula 19]

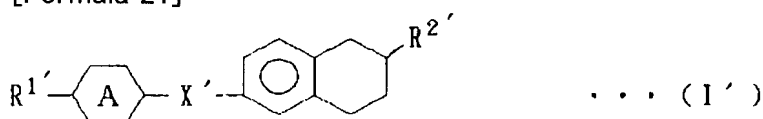


** can be mentioned. Moreover, in the case of the benzene ring, as a substituent, halogen atoms (for example, a fluorine, chlorine, an iodine atom, etc.), the cyano group, etc. may replace, and a fluorine atom is mentioned especially as a desirable halogen atom. moreover [Formula 20]

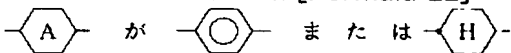


** -- even if the same, you may differ As m, 1 or 2 are desirable and 0 or 1 are desirable as n. The case where especially m is [n] 0 in 1 is desirable.

[0006] the above -- a desirable compound is expressed with the following general formula (I') [Formula 21]



R1' shows the alkyl group, the alkoxy group, halogen atom, or cyano group of carbon numbers 3-8 according to the shape of a straight chain among [formula, and R2' shows the alkyl group of carbon numbers 1-4. [Formula 22]



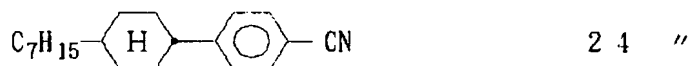
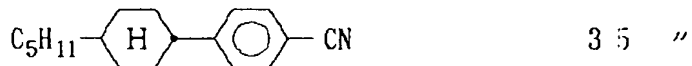
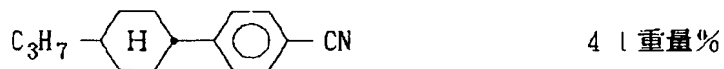
] ***** and X' indicate carboxylate combination or methylene oxy-combination to be [0007] While the compound of this invention has high physical chemical stability and a stable nematic phase is shown, it has the feature that a refractive-index anisotropy (deltan) is small. Therefore, the compound of this invention can be used as one useful component in building liquid crystal constituents, such as a liquid crystal flat-panel display of a TFT drive.

[0008] The compound of this invention can be independently used as a liquid crystal compound, and can reinforce the liquid crystal activity of other liquid crystal mixture by adding into the liquid crystal mixture of further others. Since the liquid crystal compound of this invention is conventionally excellent in compatibility with liquid crystal compounds, such as a well-known liquid crystal compound, for example, an ester system, an ether system, a carbonyl system, a biphenyl system, a phenylcyclohexane system, and a heterocycle system, it can build the liquid crystal constituent which shows the property which was excellent by carrying out addition combination to these liquid crystal compounds.

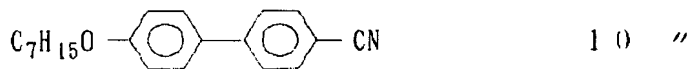
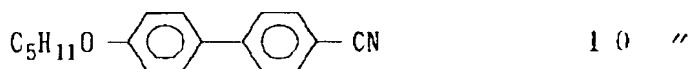
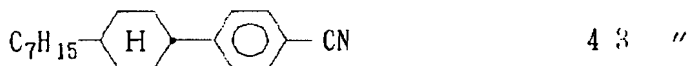
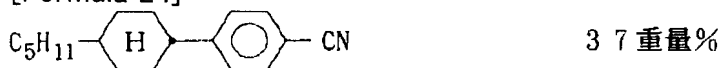
[0009] as the liquid crystal mixture which can add the compound of this invention -- for example, "Flussige Krislalle in Taballen" I&II VEB Verlag, Leipzig The nematic liquid crystal stated to a "liquid crystal device handbook" (the volume on 142nd committee of Japan Society for the Promotion of Science, Nikkan Kogyo Shimbun Ltd.) or "full color liquid crystal display technology" (the volume on Triceps publication section, Triceps, Inc.), a commercial nematic-liquid-crystal compound, etc. are mentioned. The addition of the compound of this invention in that case is usually 5% - about 20% preferably 0.5% to about 50%. As liquid crystal mixture which can add the compound of this invention, mixture with A, B, C, D, and the composition E Becoming can be mentioned. Moreover, mixed liquid crystal ZLI-1565 (Merck Co. make) of marketing etc. is mentioned.

[Liquid crystal mixture A]

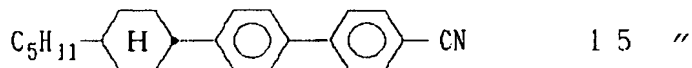
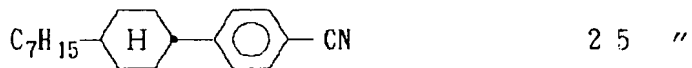
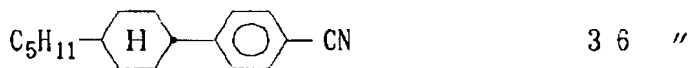
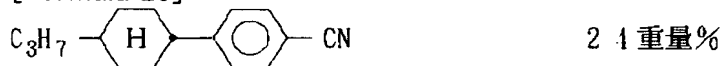
[Formula 23]



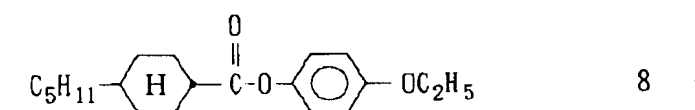
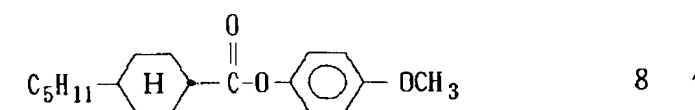
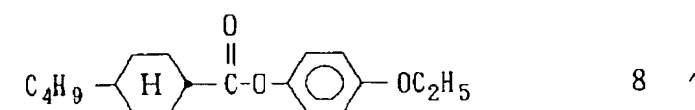
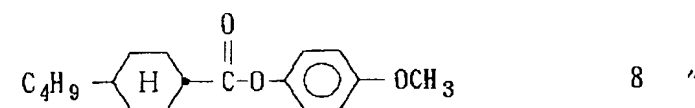
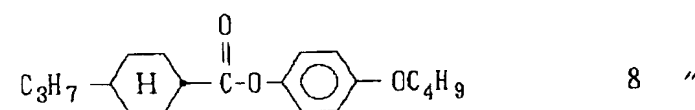
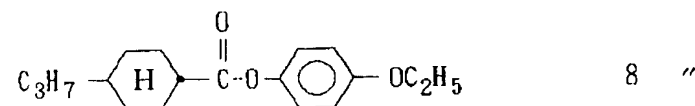
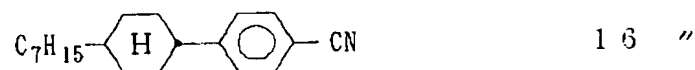
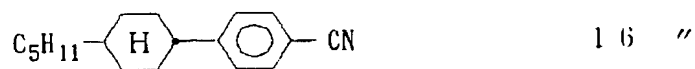
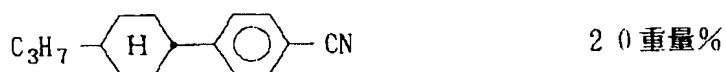
[Liquid crystal mixture B]
[Formula 24]



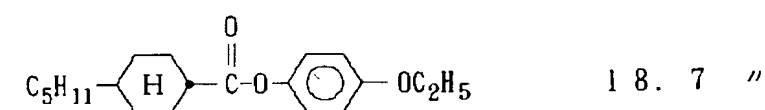
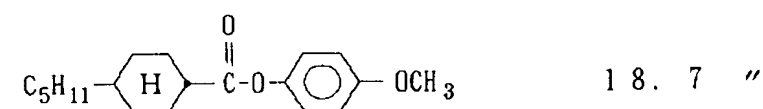
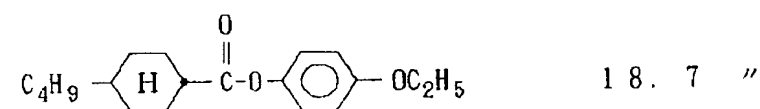
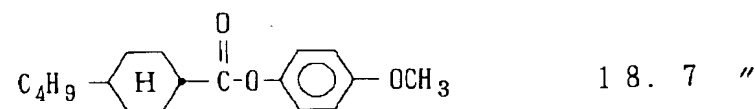
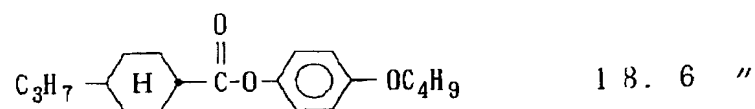
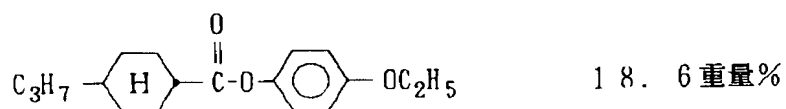
[Liquid crystal mixture C]
[Formula 25]



[Liquid crystal mixture D]
[Formula 26]

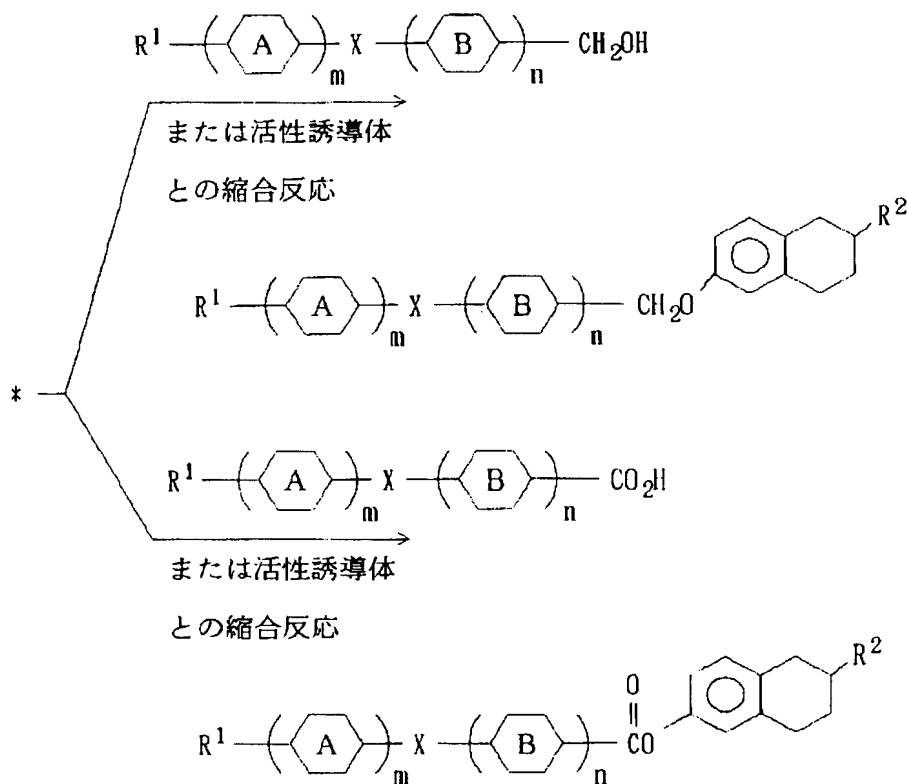
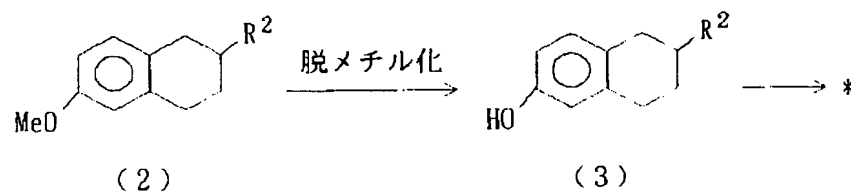
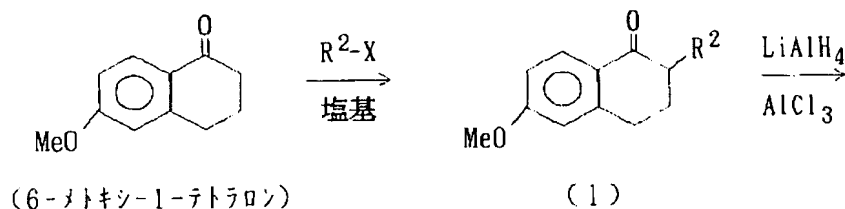


[Liquid crystal mixture E]
[Formula 27]



[0010] The manufacturing method of a compound expressed with the general formula (I) of this invention below is explained about a typical example. this invention is not limited by these methods.

The example of manufacture. [Formula 28]



Intermediate field (3) are easily manufactured in the above-mentioned synthetic path. That is, suitable alkyl halide is made to act on commercial 6-methoxy-1-tetralone under base existence, an alkyl group is introduced into the alpha-position activity methylene of a carbonyl group, and a compound (1) is obtained. If a reaction is not checked as a reaction solvent, using strong bases, such as a lithium diisopropyl amide (load accumulator direct), n-butyl lithium (n-BuLi), and a sodium hydride (NaH), as a base, it is good anything, for example, solvents, such as ether system solvents (diethylether, tetrahydrofuran, etc.), DMF and DMSO, and HMPA, are desirable. Although reaction temperature is used from -78 degrees C to room temperature grade, choosing it suitably, -20 to 0-degree-C grade is desirable. reaction time -- usually -- it is 10 minutes - 2 hours more preferably for 10 minutes to 24 hours for 5 minutes to 72 hours

[0011] The intermediate field (1) manufactured as mentioned above are given to reduction reactions (for example, reduction by the lithium-hydride aluminum-aluminum chloride, catalytic

reduction, a Wolff Kishner reduction, a clemmensen reduction, etc.), and it guides to 2 and 6-G substitution tetralin system compound (2) which changes a carbonyl group into a methylene group and is made into the purpose.

[0012] Subsequently, this compound (2) is given to the demethylation reactions (for example, heating in HBr-AcOH, heating under the NaSCH₃ existence in DMF, heating under the alkyl mercaptan-Lewis-acid existence in an organic solvent, etc.) of a conventional method, and it guides to a phenol nature compound (3).

[0013] Thus, the compound (I) of this invention made into the purpose can be manufactured by making the compounded phenol nature compound (3), an alcoholic component compound, or its activity derivative (for example, an organic sulfonate derivative, a halogen derivative) condense under suitable condensing-agent existence. As a condensing agent, inorganic bases and organic strong bases, such as diethyl ester azodicarboxylate (DEAD), triphenyl phosphine (PPh₃) and potassium carbonate, and a sodium hydride, are mentioned. If a reaction is not checked as a reaction solvent, any are sufficient and it may be necessary to use it. As an example of representation of an alcoholic component compound (the activity derivative), p-substitution benzyl alcohol (p-substitution benzyl organic sulfonate, p-substitution benzyl halide) is mentioned. As p-substitution benzyl alcohol, specifically p-cyano benzyl alcohol, p-alkoxy benzyl alcohol () [an example p-methoxy,] [p-ethoxy **] Benzyl alcohol, such as p-propoxy, p-butoxy, p-pentyloxy, and p-hexyloxy, the example (p-methyl, p-ethyl, and p-propyl --) of p-alkyl benzyl alcohol [Benzyl alcohol], such as p-butyl, p-pentyl, and p-hexyl, p-fluoro benzyl alcohol, p-chloro benzyl alcohol, p-BUROMO benzyl alcohol, and p-iodine benzyl alcohol are mentioned. Specifically as a reaction solvent, hydrocarbons, halogenated hydrocarbons, ether (diethylether, a tetrahydrofuran, dioxane, etc.), ethyl acetate, an acetonitrile, a dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), etc. are mentioned. The range of it is usually -78 degrees C - 150 degrees C, and although reaction temperature is chosen suitably, its 0 degree C - 80 degree-C grade is desirable. reaction time -- usually -- it is 10 minutes - 2 hours more preferably for 10 minutes to 24 hours for 5 minutes to 72 hours

[0014] Moreover, the compound (I) of this invention made into the purpose can be manufactured by giving a phenol nature compound (3), a carboxylic-acid component compound, or its activity derivatives (for example, acid halide etc.) to a condensation reaction under existence of the suitable condensing agent (it being [in the case of a carboxylic acid] a base as a proton acid and an activity derivative in the case of a carboxylic-acid halogenide) which is among a suitable solvent. As an example of representation of a carboxylic-acid component compound (the activity derivative), p-substitution benzoic acid (p-substitution benzoic-acid halide) is mentioned. Specifically as a p-substitution benzoic acid, p-cyano benzoic acid, a p-alkoxy benzoic acid, p-alkyl benzoic acid, p-fluoro benzoic acid, para chlorobenzoic acid, p-BUROMO benzoic acid, and p-iodine benzoic acid are mentioned. As a proton acid, strong acid nature ion exchange resin, such as organic sulfonic acids, such as inorganic acids, such as a sulfuric acid, a hydrochloric acid, and perchloric acid, p-toluenesulfonic acid, a benzenesulfonic acid, a trifluoromethane sulfonic acid, and methansulfonic acid, or Amberlyst, can be used, for example. Moreover, as an organic solvent, hydrocarbons, halogens (hexane, benzene, toluene, etc.) hydrocarbons (chloroform, a methylene chloride, a carbon tetrachloride, 1, 2-dichloroethane, etc.), ether (diethylether, a tetrahydrofuran, dioxane, etc.), ethyl acetate, an acetonitrile, a dimethylformamide, etc. can be used, for example.

[0015] A condensing agent well-known as a condensing agent used for the condensation reaction of a carboxylic acid and a phenol nature compound (3), For example, N and N-dicyclohexylcarbodiimide (DCC), the Mukoyama reagent represented with 1-methyl-2-halo pyridinium iodide, The combination of the diethyl ester (DEAD) of an azo dicarboxylic acid, and a triphenylphosphine (Ph₃ P) (the so-called Mitsunobu reagent), or a triphenylphosphine -- a jib -- there are activation reagents, such as ROMIDO, and the reaction of a carboxylic acid and a phenol nature compound can also be advanced using these

[0016] These methods 1975 For example, journal ORUGA nick chemistry, 27, 4675 (1962):Tetrahedron Letters, 1978, 4475:chemistry Letters, 1045 : Chemistry Letters, 1976, 13: 50 Pre teens chemical saucer IATI Japan, 1863 (1977), 16 Pre teens chemical saucer IATI Japan,

40, 2380(1967):synthetic handicap NYUKESHON, 1423 (1986): It is indicated by synthetic handicap NYUKESHON and 16,659 (1986).

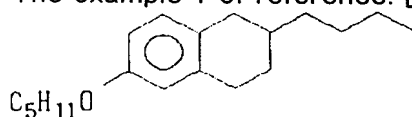
[0017] Moreover, as a base in the case of using a carboxylic-acid halogenide for condensation with a phenol nature compound (3) as an activity derivative of a carboxylic acid, organic bases, such as inorganic bases, such as potassium carbonate and a sodium carbonate, and a pyridine, a triethylamine, are used suitably. If a reaction is not checked as a reaction solvent, any are sufficient and it is not necessary to use it. Specifically as a reaction solvent, hydrocarbons, halogenated hydrocarbons, ether (diethylether, a tetrahydrofuran, dioxane, etc.), ethyl acetate, an acetonitrile, a dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), etc. are mentioned. Reaction temperature is usually the range of -78 degrees C - 150 degree-C grade, and although it is chosen suitably, its 0 degree C - 80 degree-C grade is desirable. reaction time -- usually -- it is 10 minutes - 2 hours more preferably for 10 minutes to 24 hours for 5 minutes to 72 hours

[0018] Separation refining of the specified substance (1) generated by the above-mentioned method can be carried out from reaction mixture using meanses, such as a separation refining means, for example, extraction, by which it is usually used, ****, a column chromatography, liquid chromatography, and recrystallization.

[0019]

[Example] Although an example explains this invention below, it is not limited to this.

The example 1 of reference. [Formula 29]



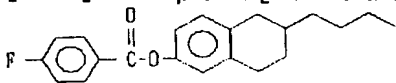
100ml of tetrahydrofuran solutions of 0.11 mols of load accumulator directs (lithium diisopropyl amide) was ice-cooled, and 6-methoxy-1-tetralone 17.6g (0.10 mols) was added. After stirring for 20 minutes, 60ml of clo chill star's picture 67.5g (0.50 mols) HMPA (hexamethylphosphoric triamide) solutions was dropped. After the dropping end, it returned to the room temperature and stirred for 2 hours. Reaction mixture was opened in water, the ether extracted, silica gel chromatography refining (expansion solvent : ethyl acetate / hexane = 5/95) was carried out to the residue after condensing an ether layer, and 6-methoxy-2-butenyl-1-tetralone 11.8g was obtained. 16.0g (0.12 mols) of anhydrous aluminum chlorides was dissolved in dryness ether 150ml under ice-cooling, lithium-hydride aluminum hydride 4.56g (0.12 mols) was added, and it stirred for 10 minutes. Ketone 6.90g (0.03 mols) obtained in the top was added calmly, and it returned to the room temperature, and for 30 minutes, after stirring, reaction mixture was carefully opened in dilute hydrochloric acid, and liquids were separated. A silica gel chromatography (expansion solvent : ethyl acetate / hexane = 2/98) refines the residue after condensing an ether layer, and it is a 6-butenyl-2-methoxy. - 5, 6, 7, and 8-tetrahydronaphthalene 6.60g was obtained. Obtained tetrahydronaphthalene 6.40g (0.0296 mols) was dissolved in methanol 60ml, palladium carbon 0.5g was added 5%, and the contact hydrogen reduction was carried out by the ordinary temperature ordinary pressure. A catalyst is ****(ed), a filtrate is condensed and it is a 6-butyl-2-methoxy. - 5, 6, 7, and 8-tetrahydronaphthalene 6.57g was obtained. 6.50g (0.0298 mols) of acquired methoxy objects was dissolved in 120ml of acetic acids, 20ml of hydrobromic acids was added 47%, and 1 evening heating reflux was carried out. Reaction mixture was condensed, the residue was opened in water, and the ether extracted. An ether layer is condensed, and it often dries and is 6-butyl-2-hydroxy. - 5, 6, 7, and 8-tetrahydronaphthalene 5.90g was obtained. 0.5g (2.45mm mol) of hydroxy objects and obtained n-amyl bromide 1.85g (12.3mm mol) were added to dimethyl sulfoxide 15ml, 0.12g (2.94mm mol) of sodium hydrides was added little by little 60%, and it stirred for 30 minutes at 70 degrees C. Reaction mixture was opened in water, the ether extracted, after condensing an ether layer, the silica gel chromatography (expansion solvent : ethyl acetate / hexane = 2/98) refined the residue, and 0.22g (32.8%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta:6.93 (d, 1H), 6.65 (dd, 1H), 6.59 (brs, 1H) and 3.88 (t, 2H), 2.84-2.63 (m, 2H), 2.47-2.23 (m,

1H), 1.96-0.79 (m, 22H)

[0020] Example 1. [Formula 30]

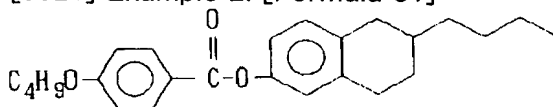


0.5g (2.45mmol) of hydroxy objects acquired in the example 1 of reference -- dichloromethane 15ml -- it dissolved in inside, triethylamine 1.24g (12.3mmol) was added, p-fluoro benzoyl chloride 0.47g (2.94mmol) was added small quantity every, and it stirred at the room temperature for 1 hour. A small amount of dilute hydrochloric acid was added to reaction mixture, it extracted by the dichloromethane, the silica gel chromatography (expansion solvent : ethyl acetate / hexane = 10/90) refined the residue after condensing an organic layer, and 0.63g (78.8%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta: 8.20 (m, 1H) and 7.27-7.04 (m, 2H), 6.91 (m, 1H), 2.93-2.62 (m, 2H), 2.56-2.27 (m, 1H), 2.01-1.08 (m, 13H), and 1.01-0.70 (m, 3H)

[0021] Example 2. [Formula 31]

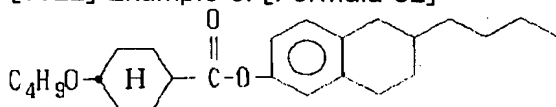


p-(n-butoxy)- Heating reflux was carried out at 80 degrees C for 2 hours, adding and stirring thionyl chloride 3ml to 0.8g (4.12mmol) of benzoic acids. Vacuum concentration of the toluene after a reaction end was added and carried out. 0.5g [of hydroxy objects] (2.45mmol) and triethylamine 1.24g (12.3mmol) obtained in the example 1 of reference was added to tetrahydrofuran 15ml, and the acid chloride obtained in the top was dropped little by little. It stirred at 80 degrees C after dropping for 2 hours, reaction mixture was condensed, silica gel chromatography (expansion solvent : chloroform) refining of the residue was carried out, and 0.52g (55.8%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta: -- 8.13 (d, 2H), 7.08 (d, 1H), and 7.03-6.86 (m, 4H), 4.03 (t, 2H), 2.94-2.67 (m, 2H), 2.54-2.27 (m, 1H), 1.98-1.14 (m, 14H), and 1.12-0.83 (m, 6H)

[0022] Example 3. [Formula 32]

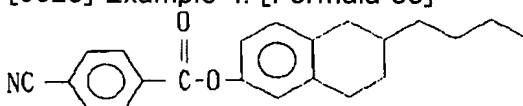


Heating reflux was carried out at 80 degrees C for 2 hours, adding and stirring thionyl chloride 3ml to 0.68g (3.69mmol) of trans-4-n-cyclohexane carboxylic acid. Vacuum concentration of the toluene was added and carried out after the reaction end. 0.5g [of hydroxy objects] (2.45mmol) and triethylamine 1.24g (12.3mmol) obtained in the example 1 of reference was added to tetrahydrofuran 15ml, and the acid chloride obtained in the top was dropped little by little. It stirred at 80 degrees C after dropping for 2 hours, and the reaction end postprecipitation Mr. object was carried out the ** exception, the filtrate was condensed, silica gel chromatography (expansion solvent : chloroform) refining of the residue was carried out, and 0.53g (58.4%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta: -- 7.02 (d, 1H), 6.76 (m, 2H), 2.88-2.63 (m, 3H), 2.52-2.27 (m, 2H), 2.18-2.03 (m, 2H), and 1.98-0.72 (m, 28H)

[0023] Example 4. [Formula 33]



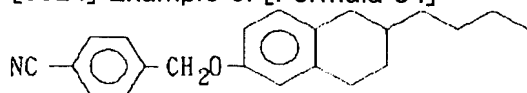
0.5g [of hydroxy objects] (2.45mmol) and triethylamine 1.24g (12.3mmol) obtained in the

example 1 of reference was added to THF 20ml, p-cyano benzoyl chloride 0.61g was added little by little, and heating reflux was carried out, stirring at 80 degrees C for 1.5 hours. Precipitate was carried out the ** exception from reaction mixture, a small amount of dilute hydrochloric acid was added to the filtrate, it extracted by the dichloromethane, the organic layer was condensed, silica gel chromatography (expansion solvent : chloroform) refining of the residue was carried out, recrystallization was performed from the hexane, and 0.5g (61.2%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta: 8.29 (d, 2H), 7.82 (d, 2H), 7.12 (d, 1H) and 6.93 (m, 2H), 2.95-2.79 (m, 3H), 2.48-2.31 (m, 1H), 2.03-1.22 (m, 9H), 0.98-0.87 (m, 3H)

[0024] Example 5. [Formula 34]

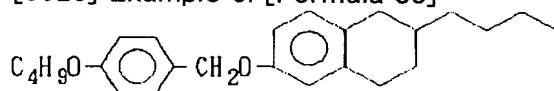


0.5g [of hydroxy objects] (2.45mmol) and alpha-BUROMO-p-torr nitril 2.4g (12.3mmol) obtained by dimethyl sulfoxide 20ml in the example 1 of reference was dissolved, 0.12g (2.94mmol) of sodium hydrides was added little by little 60%, and it stirred at 70 degrees C for 1.5 hours. Reaction mixture was condensed, silica gel chromatography (expansion solvent : ethyl-acetate / hexane = 25/75) refining of the residue was carried out, and 0.23g (29.4%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta: 7.67 (d, 2H), 7.54 (d, 2H), 6.98 (d, 1H), 6.70 (m, 2H) and 5.08 (s, 2H), 2.89-2.54 (m, 3H), 2.51-2.22 (m, 1H), 2.09-0.72 (m, 12H)

[0025] Example 6. [Formula 35]



0.64g (3.68mmol) of diethyl azodicarboxylate was dropped dissolving and stirring 0.5g [of hydroxy objects acquired from the example 1 of reference] (2.45mmol), and n-butoxy benzyl alcohol 2.21g (12.3mmol), and triphenyl phosphine 0.96g (3.68mmol) to dichloromethane 20ml, and it stirred at the room temperature one whole day and night. Reaction mixture was condensed, the silica gel chromatography (expansion solvent : ethyl acetate / hexane = 10/90) refined the residue, and 0.26g (29.0%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

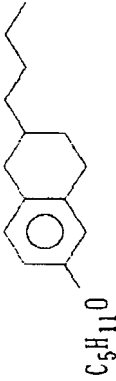
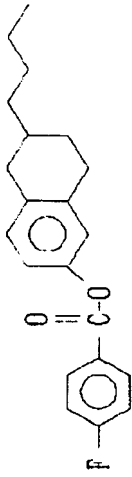
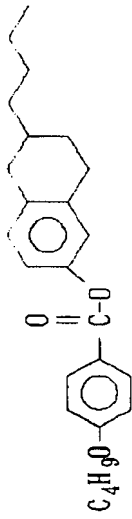
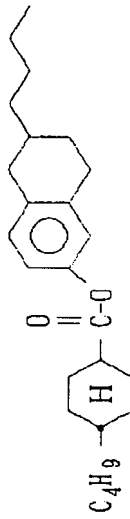
delta: 7.33 (d, 2H), 6.96 (d, 1H), 6.88 (d, 2H), 6.73 (m, 2H), 4.94 (s, 2H) and 3.97 (t, 2H), 2.86-2.63 (m, 2H), 2.47-2.22 (m, 1H), 1.97-1.13 (m, 14H), 1.08-0.78 (m, 6H)

[0026] The phase transition temperature of the compound obtained in the example of the physical-properties measurement above-mentioned reference and the example and the judgment of a phase were performed by using together the visual observation and the differential scanning calorimeter (DSC) by the polarization microscope. Moreover, about delta n and delta epsilon, it measured according to the reference method. The obtained result is shown in Table 1.

[0027]

[Table 1]

表 - 1

例	構造式	相転移温度 (°C)	Δn	$\Delta \epsilon$
参考例 1		oil	—	—
実施例 1		\rightleftharpoons N — I >-30 21.5	0.081	0.35
実施例 2		K \rightleftharpoons N — I 38.0 89.6	0.076	(0.003)
実施例 3		K \rightleftharpoons N — I 14.0 60.5	0.051	微少

[0028]
[Table 2]

表 - 1 (つづき)

実施例 4		$\begin{array}{c} 88.2 \\ \text{K} \rightleftharpoons \text{N} \text{---} \text{I} \\ 106.0 \quad 128.9 \end{array}$	0.120	4.21 (-10°C) 4.98 (-30°C)
実施例 5		$\begin{array}{c} \text{K} \text{---} \text{N} \text{---} \text{I} \\ 43 \text{---} 52 \end{array}$		
実施例 6		$\begin{array}{c} \text{K} \rightleftharpoons \text{N} \text{---} \text{I} \\ 26.9 \quad 26.9 \end{array}$	0.07	

(注) 液晶相などの各相は、次の記号で示した。

I : 等方相 ; N : ネマチック相 ; K : 結晶相

[0029]

[Effect of the Invention] 2-alkyl-6-substitution which is the compound of this invention - 1, 2, 3, and 4-tetrahydronaphthalene derivative is a new compound, and in case it prepares the liquid crystal constituent used for a liquid crystal flat-panel display etc., it is one useful component. That is, this compound is chemically [physically] stable, and shows stably a desirable liquid crystal phase (nematic-liquid-crystal phase), and its compatibility with liquid crystal compounds, such as many of other liquid crystal compounds, for example, an ester system, an ether system, a carbonyl system, a biphenyl system, a phenylcyclohexane system, and a heterocycle system, is good, it adds to these compound and its liquid crystal constituent, and an N-I point can be raised or it can improve other physical properties. Thus, this invention offers a compound useful as one component in building the liquid crystal constituent used for a liquid crystal flat-panel display etc.

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Bibliography.

- (19) [Country of Issue] Japan Patent Office (JP)
(12) [Official Gazette Type] Open patent official report (A)
(11) [Publication No.] JP,6-256284,A.
(43) [Date of Publication] September 13, Heisei 6 (1994).
(54) [Title of the Invention] The liquid crystal constituent containing the 2-cyano-6-substitution-3, 4-dihydro(or 1, 2, 3, 4-tetrahydro) naphthalene derivatives, those manufacturing methods, and this derivative.
(51) [The 5th edition of International Patent Classification]

C07C255/47	9357-4H.
253/30	
327/24	7106-4H.
327/26	7106-4H.
C07D239/26	8615-4C.
239/28	8615-4C.
239/34	8615-4C.
239/38	8615-4C.
C09K 19/32	9279-4H.
19/34	9279-4H.
G02F 1/13	500

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[Mode of Application] OL.

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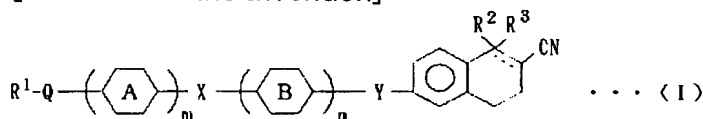
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Summary.

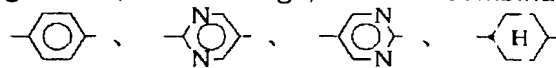
(57) [Abstract] (*****)

[Objects of the Invention] While it is chemically [physically] stable and a stable nematic phase is shown, a liquid crystal compound with a large dielectric constant anisotropy ($\Delta\epsilon$) is offered.

[Elements of the Invention]



R¹ shows an alkyl group among [formula, R² and R³ show H and a halogen atom, or they show =O by R² and R³, Q shows single bond, ether linkage, or ester combination, and A ring and B ring

may be replaced, respectively. 

*****, and X and Y shall show single bond, ester (thio) combination, methylene oxy- combination, or oxy-methylene combination, m and n shall show 0, 1, or 2, and both shall not be 0 simultaneously.] the 2-cyano-6-substitution -3 come out of and expressed, and a 4-dihydro (or 1, 2, 3, 4-tetrahydro) naphthalene derivative -- the manufacturing method of them, and a liquid crystal constituent

[Translation done.]

* NOTICES *

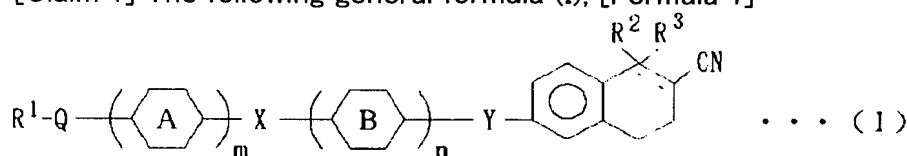
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CLAIMS

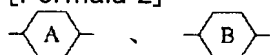
[Claim(s)]

[Claim 1] The following general formula (I), [Formula 1]

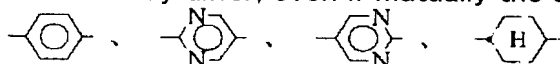


R¹ shows among [formula the alkyl group of the carbon numbers 1-14 which may be replaced, both [being another respectively or] R² and R³ show a hydrogen atom or a halogen atom, or they show =O by R² and R³, and Q shows single bond, ether linkage, or ester combination.

[Formula 2]



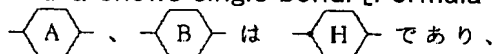
** -- it may differ, even if mutually the same, and it may be replaced, respectively [Formula 3]



*****, and X and Y show single bond, ester (thio) combination, methylene oxy-combination, or oxy-methylene combination, respectively. [Formula 4]

***** or a double bond shall be shown, m and n shall show 0, 1, or 2, respectively, and both shall not be 0 simultaneously. However, when m is 0, either Q and X are shown, at least one side shows single bond, and when n is 0, even if there are little X and Y either, one side shows single bond.] The 2-cyano-6-substitution -3 come out of and expressed, a 4-dihydro(or 1, 2, 3, 4-tetrahydro) naphthalene derivative.

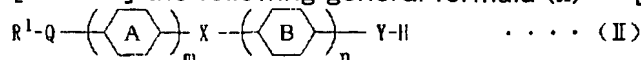
[Claim 2] The inside of a general formula (I), and R¹ A carbon number shows the alkyl group of 3-6 according to the shape of a straight chain, and it is R² and R³. Both [being another respectively or] hydrogen atoms or fluorine atoms are shown, or it is R² and R³. =O is shown and Q shows single bond. [Formula 5]



The compound according to claim 1 whose others X and Y are carboxylate combination or methylene oxy-combination, respectively, and it is 0 in 1 any of m and n they are.

[Claim 3] The compound according to claim 1 whose halogen atom is a fluorine atom.

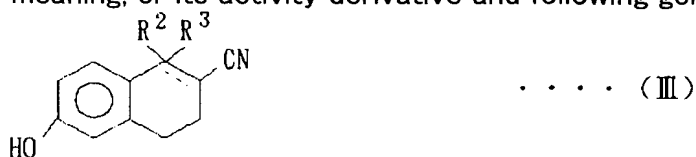
[Claim 4] the following general formula (II) ** [Formula 6]



the inside of [formula, R1, and X, Y, m and n -- and . [Formula 7]

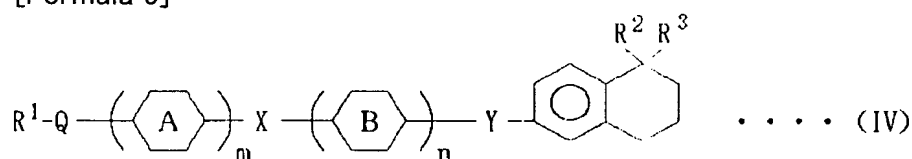


The skeleton component compound expressed with] which has ***** 1 publication and this meaning, or its activity derivative and following general formula (III), [Formula 8]



It is the manufacture method of the compound according to claim 1 characterized by giving the phenol nature compound expressed with [R2 and R3 have the above and this meaning] to a condensation reaction.

[Claim 5] The following general formula (IV)
[Formula 9]



R1, R2, R3, and Q, X, Y, A, B, m and n have claim 1 publication and this meaning among [formula.] The manufacture method of the compound according to claim 1 characterized by coming out and making the tetralone derivative expressed react with a hydroxylamine and an ethyl formate, or a sodium ethoxide.

[Claim 6] The liquid crystal constituent which contains at least one sort of a compound according to claim 1, and is characterized by the bird clapper.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

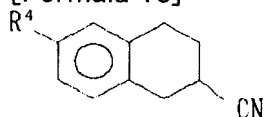
[Industrial Application] this invention relates to the liquid crystal constituent which shows a liquid crystal phase and contains at least one sort of new liquid crystal compounds and them of low viscosity.

[0002]

[Description of the Prior Art] A liquid crystal compound shows a dielectric constant anisotropy and an optical anisotropy with a liquid crystal phase. The application product which there are a nematic-liquid-crystal phase, a smectic-liquid-crystal phase, and cholesteric-liquid-crystal equality in a liquid crystal phase, among these used the nematic-liquid-crystal phase is put in

practical use most widely. That is, the application product using these properties is developed by sign display rows including modulated light glass to flat-panel displays, such as a calculator, a clock, and a word processor, etc., it is various with progress of the latest electronics field, and the development is remarkable. the difference in a method which makes a liquid crystal compound drive -- a dynamic scattering type (DS type) -- it is twisted and is classified into a super-[a nematic type (TN type) and] torsion nematic type (STN type), a guest-host type (GH type), etc. Stability [as opposed to / naturally / physicochemical stability especially heat, light, moisture, air, etc. in the liquid crystal material used for these] is required. Moreover, liquid crystal material shows a desired liquid crystal phase by the broad temperature requirement including a room temperature as it can do, and it must be satisfied [with practical use level] of physical properties according to the purpose, such as operating voltage and responsibility. That is, in order for threshold voltage and a saturation voltage required for making a liquid crystal display element drive generally to carry out a thing low if possible and a speed of response early, the method of a low has the as much as possible good viscosity of liquid crystal material. 6-substitution proposed from the former - As the additive with which a 1, 2, 4, 3, and 4-tetrahydronaphthalene-2-carbonitrile (JP,56-57754,A and a structure expression are a lower formula) increases the dielectric anisotropy ($\Delta\epsilon$) of a nematic-liquid-crystal constituent. 6-cyano-2-(4-alkyl phenethyl) naphthalene (JP,61-246158,A and a structure expression are a lower formula) and 6-cyano-2-substitution naphthalene (JP,61-268661,A and a structure expression are a lower formula) are useful as a useful and big constituent of a nematic-liquid-crystal constituent of a refractive-index anisotropy (Δn).

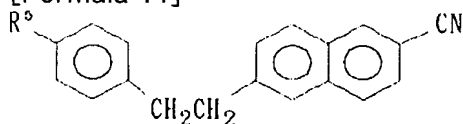
[Formula 10]



(JP,56-57754,A)

(R4 : The alkyl group or alkoxy group of carbon numbers 3-10)

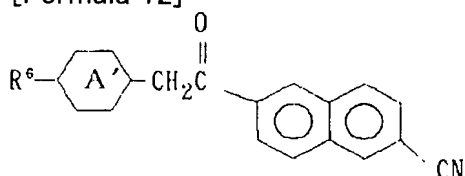
[Formula 11]



(JP,61-246158,A)

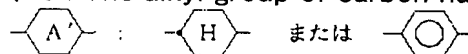
(R5 : Alkyl group of carbon numbers 1-10)

[Formula 12]



(JP,61-268661,A)

(R6 : The alkyl group of carbon numbers 1-10) [Formula 13]



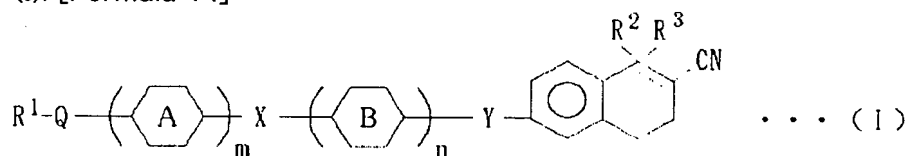
[0003]

[Problem(s) to be Solved by the Invention] However, it is impossible to fill many above-mentioned physical properties with an item compound, and the present condition is having mixed several sorts of liquid crystal compounds, and the non-liquid crystal compound, and having gained practical demand characteristics. It is very important to develop the item compound which has many best possible physical properties in building the liquid crystal constituent to which these practical demand characteristics is satisfied. In case the purpose of this invention

develops such a practical liquid crystal constituent, it is offering a useful new liquid crystal compound.

[0004]

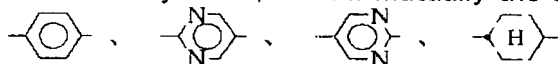
[Means for Solving the Problem] The summary of this invention is the following general formula (I). [Formula 14]



R¹ shows among [formula the alkyl group of the carbon numbers 1-14 which may be replaced, and both [being another respectively or] R² and R³ show [both] a hydrogen atom or a halogen atom, or =O is shown, and Q shows single bond, ether linkage, or ester combination. [Formula 15]



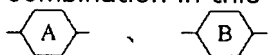
** -- it may differ, even if mutually the same, and it may be replaced, respectively [Formula 16]



*****, and X and Y show single bond, ester (thio) combination, methylene oxy-combination, or oxy-methylene combination, respectively. [Formula 17]

***** or a double bond shall be shown, m and n shall show 0, 1, or 2, respectively, and both shall not be 0 simultaneously. However, when m is 0, either Q and X are shown, at least one side shows single bond, and when n is 0, even if there are little X and Y either, one side shows single bond.] It comes out, and is in the 2-cyano-6-substitution -3 expressed and a 4-dihydro(or 1, 2, 3, 4-tetrahydro) naphthalene derivative, and the liquid crystal constituent containing the manufacture method of this compound and one or more sorts of these compounds is included.

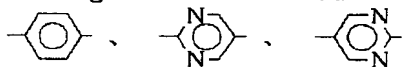
[0005] It sets to the compound expressed with the aforementioned general formula (I) concerning this invention, and is R¹. The alkyl group of the carbon numbers 1-14 which may be replaced is shown. These alkyl groups may be any of a straight chain or branching. specifically For example, a methyl, ethyl, a propyl, butyl, a pentyl, a hexyl, a heptyl, In straight chain-like alkyl group rows, such as an octyl, a nonyl, a desyl, a undecyl, a dodecyl, tridecyl, and tetradecyl, an isopropyl, An isobutyl, sec-butyl, tert-butyl, an isopentyl, neopentyl, The alkyl group of letters of branching, such as a tert-pentyl, an iso hexyl, 1-methyl pentyl, 2-methyl pentyl, 5-methyl hexyl, 2 and 3, a 5-trimethyl hexyl, 2 and 7, a 8-trimethyl desyl, and a 4-ethyl-5-methyl nonyl, can be mentioned. R¹ If it attaches, the alkyl group of 3-6, for example, a propyl, butyl, a pentyl, and a hexyl have a desirable carbon number especially at the shape of a straight chain. R² and R³ A hydrogen atom or halogen atoms (for example, a fluorine, chlorine, an iodine atom, etc.) are shown in according to, respectively, or it is R². R³ One hydrogen atom or a halogen atom is shown, or it is R² and R³. Although =O is shown, as a halogen atom, a fluorine atom is desirable. Although single bond, ester (thio) combination, methylene oxy-combination, or oxy-methylene combination is included about the combination in a skeleton shown by X and Y, respectively, single bond and carboxylate combination are desirable especially. Any are sufficient although there are order ester combination and reverse ester combination about the carboxylate combination in this case. Further, [Formula 18]



As the ring come out of and shown [Formula 19]



although ** is mentioned -- desirable [Formula 20]



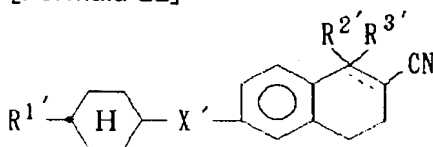
** can be mentioned. Moreover, in the case of the benzene ring, as a substituent, the halogen, the cyano group, etc. may replace and a fluorine atom is mentioned especially as a desirable halogen atom. moreover [Formula 21]



** -- even if the same, you may differ

[0006] Especially the desirable mode of this invention is a compound expressed with the following general formula (I').

[Formula 22]



[R1' is the alkyl group of carbon numbers 3-6 in the shape of a straight chain among a formula, both [being another respectively or] R2' and R3' show a hydrogen atom or a fluorine atom, or show =O by R2' and R3', and X' is carboxylate combination or methylene oxy-combination.]

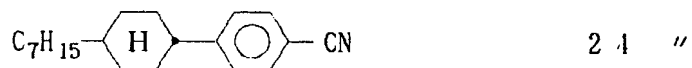
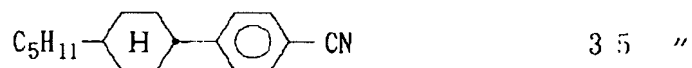
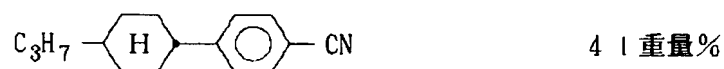
[0007] While the compound of this invention has high physical chemical stability and a stable nematic phase is shown, about a certain compound, it has the feature that a dielectric constant anisotropy ($\Delta\epsilon$) is large. Therefore, the compound of this invention can be used as one useful component in being an additive effective in low-battery-izing of a liquid crystal constituent, and building a practical liquid crystal constituent about threshold voltage and a saturation voltage required for making a liquid crystal display element etc. drive. The compound of this invention can be independently used as a liquid crystal compound, and can reinforce the liquid crystal activity of other liquid crystal mixture by adding into the liquid crystal mixture of further others.

[0008] Since the liquid crystal compound of this invention is conventionally excellent in compatibility with liquid crystal compounds, such as a well-known liquid crystal compound, for example, an ester system, an ether system, a carbonyl system, a biphenyl system, a phenylcyclohexane system, and a heterocycle system, it can build the liquid crystal constituent which shows the property which was excellent by carrying out addition combination to these liquid crystal compounds. as the liquid crystal mixture which can add this compound -- for example, "Flussige Kristallein Tabellen" I&II VEB Verlag.Leipzig The nematic liquid crystal stated to a "liquid crystal device handbook" (the volume on 142nd committee of Japan Society for the Promotion of Science, Nikkan Kogyo Shimbun Ltd.) or "full color liquid crystal display technology" (the volume on Triceps publication section, Triceps, Inc.), a commercial nematic-liquid-crystal compound, etc. are mentioned. The addition of the compound of this invention in that case is usually 5% - about 20% preferably 0.5% to about 50%.

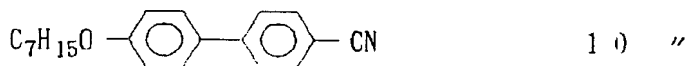
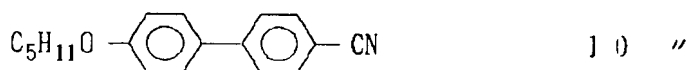
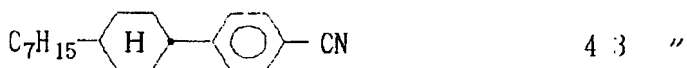
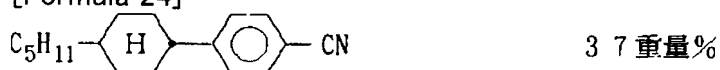
[0009] As liquid crystal mixture which can add the compound of this invention, mixture with A, B, C, D, and the composition E Becoming can be mentioned. Moreover, mixed liquid crystal ZLI-1565 (Merck Co. make) of marketing etc. is mentioned.

[Liquid crystal mixture A]

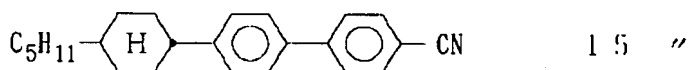
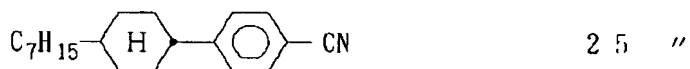
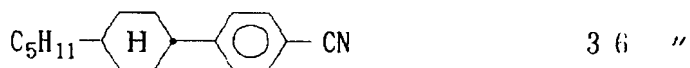
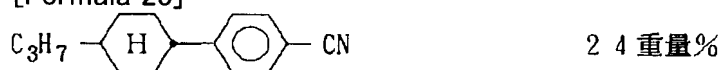
[Formula 23]



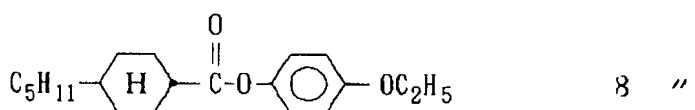
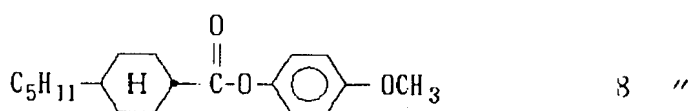
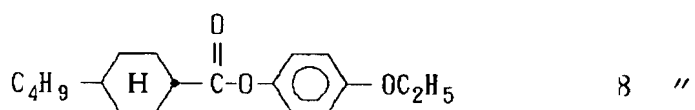
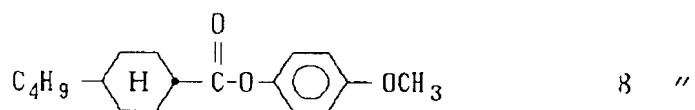
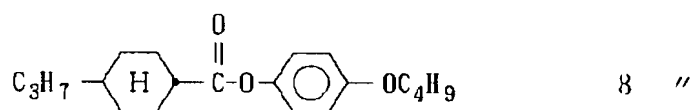
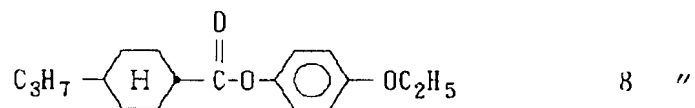
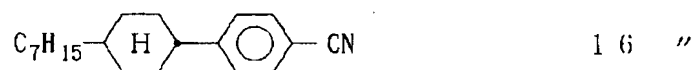
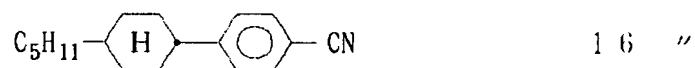
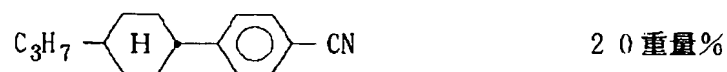
[Liquid crystal mixture B]
[Formula 24]



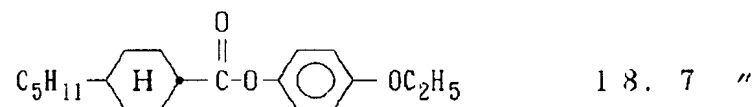
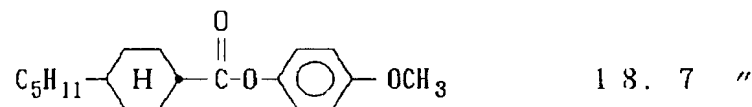
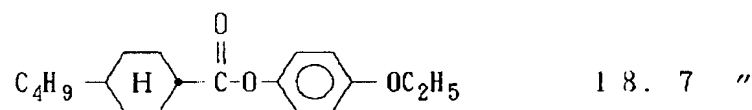
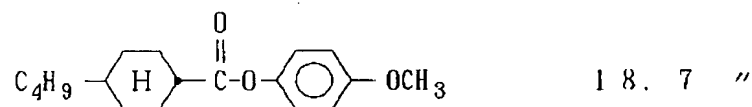
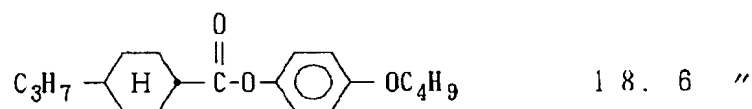
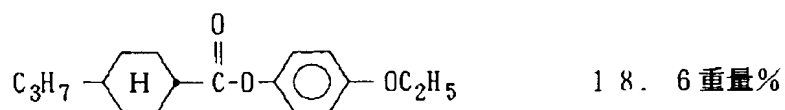
[Liquid crystal mixture C]
[Formula 25]



[Liquid crystal mixture D]
[Formula 26]

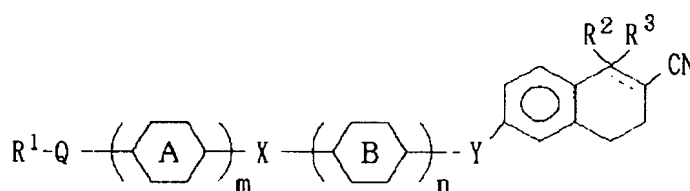
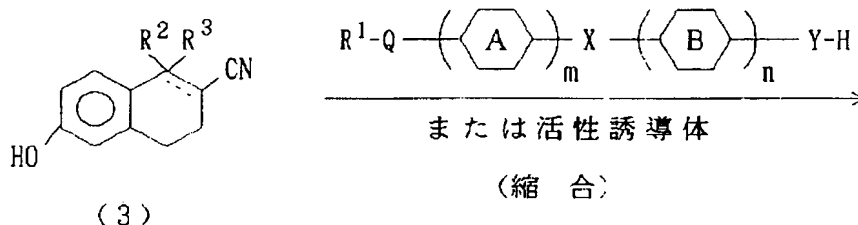
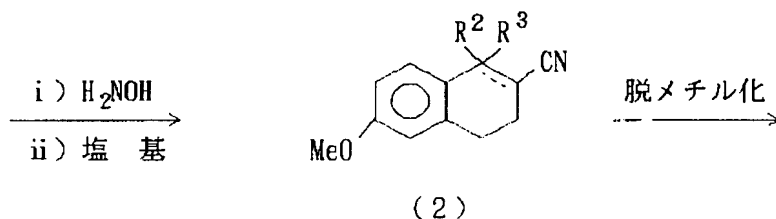
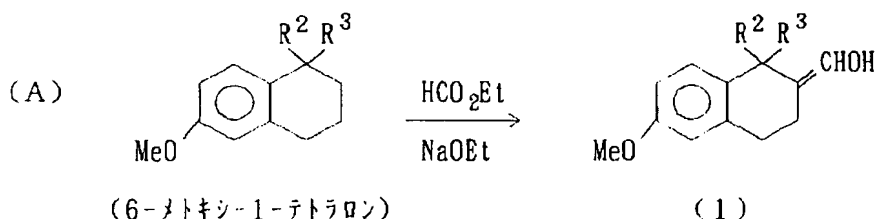


[Liquid crystal mixture E]
[Formula 27]



[0010] The manufacturing method of a compound expressed with the general formula (I) of this invention below is explained about a typical example. this invention is not limited by these methods.

The example of manufacture (A) [Formula 28]



本発明化合物 (I)

Intermediate field (2) are easily manufactured according to the method (A.Chatterjee et al., Synthesis, 1981, 449) of reference. This intermediate field (2) were given to the demethylation reactions (for example, heating in $\text{HBr}-\text{AcOH}$, heating under the existence in $[\text{NaSCH}_3]$ DMF, alkyl mercaptan-Lewis-acid processing in an organic solvent, etc.) of a conventional method, and it considered as the phenol nature compound (3). Thus, the compound (I) of this invention made into the purpose can be manufactured by making the compounded phenol nature intermediate field (3), an alcoholic component compound, or its activity derivative (for example, an organic sulfonate derivative, a halogen derivative) condense under condensing-agent existence. As a condensing agent, inorganic bases and organic strong bases, such as diethyl ester azodicarboxylate (DEAD), triphenyl phosphine (PPh_3) and potassium carbonate, and a sodium hydride, are mentioned. As long as it does not check a reaction as a reaction solvent, any are sufficient, and it may be necessary to use it. As an example of representation of an alcoholic component compound (the activity derivative), 4-substitution cyclohexyl methyl alcohol, namely, 4-alkyl cyclohexyl methyl alcohol (an example 4-methyl --) Cyclohexyl methyl alcohol, such as 4-ethyl, 4-propyl, 4-butyl, 4-pentyl, and 4-hexyl, 4-alkoxy cyclohexyl methyl alcohol (an example 4-methoxy --) 4-ethoxy **4-propoxy, 4-butoxy, 4-pentyloxy, cyclohexyl methyl alcohol, such as 4-hexyloxy, and 4-acyloxy cyclohexyl methyl alcohol (example 4-acetyloxy --) Cyclohexyl methyl alcohol, such as 4-propionyloxy, 4-butanoyloxy, 4-PENTANOIRUOKISHI, and 4-hexanoyloxy, is mentioned. Moreover, the organic sulfonates (for example, 4-alkyl cyclohexyl

methyl p-toluene sulfonate etc.) and halogen derivatives (for example, 4-alkyl cyclohexyl methyl chloride etc.) which correspond as the activity derivative, respectively are mentioned.

[0011] Specifically as a reaction solvent, hydrocarbons, halogenated hydrocarbons, ether (diethylether, a tetrahydrofuran, dioxane, etc.), ethyl acetate, an acetonitrile, a dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), etc. are mentioned. Reaction temperature is usually the range of -78 degrees C - 150 degree-C grade, and although it is chosen suitably, its 0 degree C - 80 degree-C grade is desirable. reaction time -- usually -- it is 10 minutes - 2 hours more preferably for 10 minutes to 24 hours for 5 minutes to 72 hours

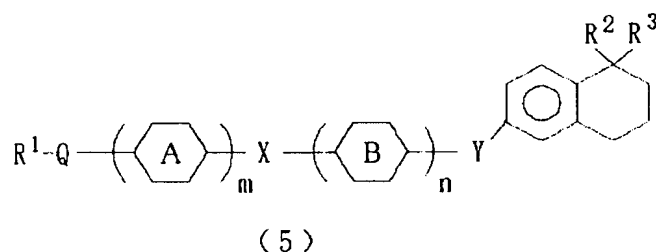
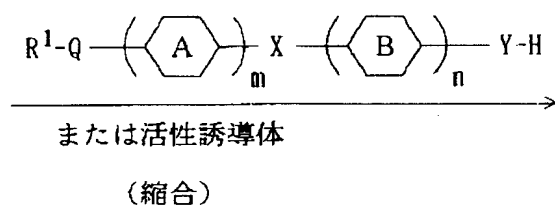
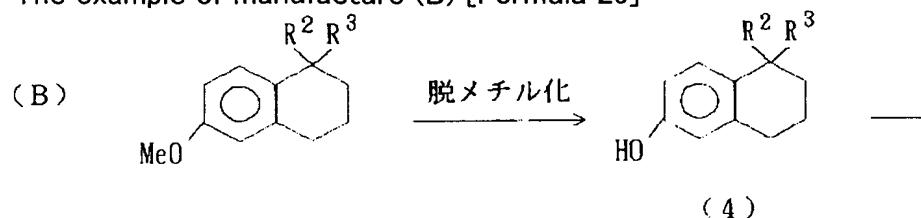
[0012] Moreover, the compound (I) of this invention made into the purpose can be manufactured by giving a phenol nature compound (3), a carboxylic-acid component compound, or its activity derivatives (for example, acid halide etc.) to a condensation reaction among a suitable solvent under existence of a suitable condensing agent (it being [in the case of a carboxylic acid] a base as a proton acid and an activity derivative in the case of a carboxylic-acid halogenide). As a proton acid, strong acid nature ion exchange resin, such as organic sulfonic acids, such as inorganic acids, such as a sulfuric acid, a hydrochloric acid, and perchloric acid, p-toluenesulfonic acid, a benzenesulfonic acid, a trifluoromethane sulfonic acid, and methansulfonic acid, or Amberlyst, can be used, for example. Moreover, as an organic solvent, hydrocarbons, halogens (hexane, benzene, toluene, etc.) hydrocarbons (chloroform, a methylene chloride, a carbon tetrachloride, 1, 2-dichloroethane, etc.), ether (diethylether, a tetrahydrofuran, dioxane, etc.), ethyl acetate, an acetonitrile, a dimethylformamide, etc. can be used, for example. A condensing agent well-known as a condensing agent used for the condensation reaction of a carboxylic acid and a phenol nature compound (3), For example, N and N-dicyclohexylcarbodiimide (DCC), the Mukoyama reagent represented with 1-methyl-2-halo pyridinium iodide, the combination (the so-called Mitsunobu reagent) of the diethyl ester (DEAD) of an azo dicarboxylic acid, and a triphenylphosphine (Ph₃P), or a triphenylphosphine -- a jib, although there are activation reagents, such as ROMIDO The reaction of a carboxylic acid and a phenol nature compound can also be advanced using these. As an example of representation of a carboxylic-acid component compound (the activity derivative), 4-substitution cyclohexane carboxylic acid, namely, 4-alkyl cyclohexane carboxylic acid (an example 4-methyl --) Cyclohexane carboxylic acid, such as 4-ethyl, 4-propyl, 4-butyl, 4-pentyl, and 4-hexyl, 4-alkoxy cyclohexane carboxylic acid () [an example 4-methoxy,] [4-ethoxy **] Cyclohexane carboxylic acid, such as 4-propoxy, 4-butoxy, 4-pentyloxy, and 4-hexyloxy, 4-acyloxy cyclohexane carboxylic acid (cyclohexane carboxylic acid, such as example 4-acetyloxy, 4-propionyloxy, 4-butanoyloxy, 4-PENTANOIRUOKISHI, and 4-hexanoyloxy) is mentioned. Moreover, the acid halides (for example, 4-alkyl cyclohexane-carboxylic-acid chloride etc.) which correspond as an example of representation of the activity derivative are mentioned.

[0013] These methods 1975 For example, journal ORUGA nick chemistry, 27, 4675 (1962):Tetrahedron Letters, 1978, 4475:chemistry Letters, 1045 : Chemistry Letters, 1976, 13: 50 Pre teens chemical saucer IATI Japan, 1863 (1977), 16 Pre teens chemical saucer IATI Japan, 40, 2380(1967):synthetic handicap NYUKESHON, 1423 (1986): It is indicated by synthetic handicap NYUKESHON and 16,659 (1986).

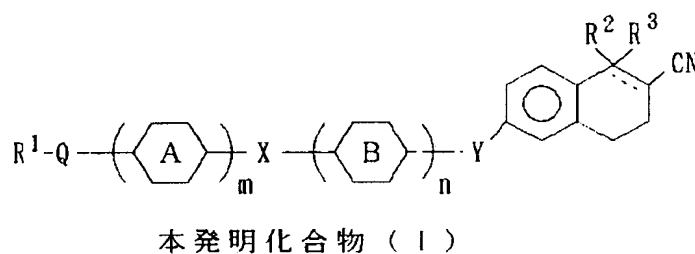
[0014] Moreover, as a base in the case of using a carboxylic-acid halogenide for condensation with a phenol nature compound (3) as an activity derivative of a carboxylic acid, organic bases, such as inorganic bases, such as potassium carbonate and a sodium carbonate, and a pyridine, a triethylamine, are used suitably. If a reaction is not checked as a reaction solvent, any are sufficient and it is not necessary to use it.

[0015] Specifically as a reaction solvent, hydrocarbons, halogenated hydrocarbons, ether (diethylether, a tetrahydrofuran, dioxane, etc.), ethyl acetate, an acetonitrile, a dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), etc. are mentioned. Although reaction temperature is usually suitably chosen in the range of -78 degrees C - 150 degree-C grade, its 0 degree C - 80 degree-C grade is desirable. reaction time -- usually -- it is 10 minutes - 2 hours more preferably for 10 minutes to 24 hours for 5 minutes to 72 hours

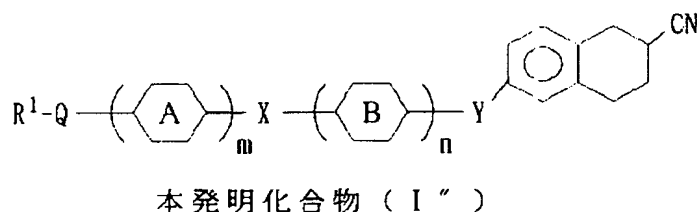
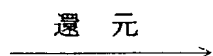
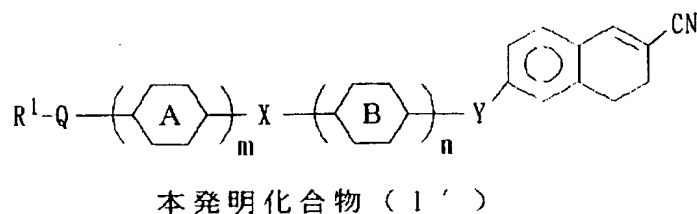
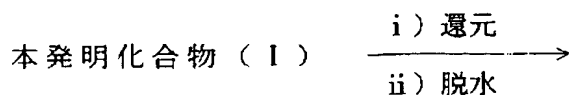
[0016] As mentioned above, although the typical manufacture method of the liquid crystal compound (I) of this invention was described, it is not limited to these methods. For example, the method shown in the following example of manufacture (B) is mentioned. The example of manufacture (B) [Formula 29]



i) $HCO_2Et/NaOEt$
 ii) H_2NOH
 iii) 塩 基

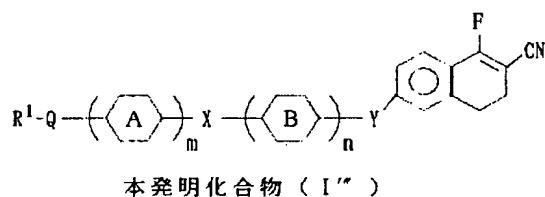
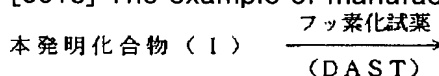


[0017] The example of manufacture (C) [Formula 30]



Thus, by choosing suitably the reduction reactions (the catalytic reduction and the Wolff Kishner reduction using catalysts, such as chemistry reduction by metal hydrides, such as a sodium borohydride and lithium-hydride aluminum, and Pd, Pt, clemmensen reduction, etc.) and dehydration [heating for example, under the dehydrating-agent existence (for example, potassium hydrogensulfate etc.) in an organic solvent] of a conventional method, the compound (I) of the compound this invention can manufacture a corresponding, related this invention compound (I' and I'').

[0018] The example of manufacture (D) [Formula 31]



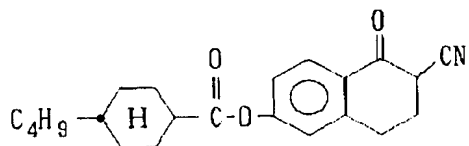
Moreover, the related this invention compound (I''') which corresponds by making a fluoridation agent [for example, dimethylamino sulfas trifluoride (DAST) etc.] act on the compound (I) of an above-mentioned this invention can be manufactured. As mentioned above, although the typical manufacturing method was described, being contained in the related this invention compound (I') which is not limited to these manufacturing methods and obtained according to each manufacturing method, and (I'') (I''') the range of this invention cannot be overemphasized.

[0019] Separation refining of specified substance compound [of this invention generated by the above-mentioned method] (I) - (I''') can be carried out from reaction mixture using meanses, such as a separation refining means, for example, extraction, by which it is usually used, ***, a column chromatography, liquid chromatography, and recrystallization.

[0020]

[Example] Although an example explains this invention in detail below, it is not limited to this.

Example 1. [Formula 32]

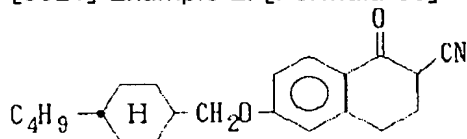


It compounded according to the example of manufacture (A). 2-cyano-6-methoxy-1-tetralone (2)8.0g (0.0398 mols) compounded by the indicated known method was first dissolved in reference [Synthesis, 449 (1981)] at dimethylformamide 150ml, sodium thio methoxide 5.0g (0.0713 mols) was added, and it stirred at 140 degrees C for 10 hours. Reaction mixture was calmly opened in cold diluted hydrochloric acid, and the ether extracted. The ether layer was condensed, it often dried and 2-cyano-6-hydroxy-1-tetralone (3)7.0g was obtained. 3.74g (0.02 mols) of phenol nature compounds and obtained triethylamine 10.12g (0.1 mols) were dissolved in the 50ml methylene chloride, acid chloride 4.04g (0.02 mols) of trans-4-butyl-cyclohexane carboxylic acid was added, and it stirred at the room temperature for 1 hour. Reaction mixture was condensed, the silica gel chromatography (expansion solvent : chloroform) refined the residue, and 2.60g of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta:8.10 (d, 1H), 7.10-7.00 (m, 2H), and 3.75 (dd, 1H) and 3.20 -3.00 (m, 2H), 2.65-2.35 (m, 3H), 2.20-2.05 (m, 2H), 2.00-1.80 (m, 2H), and 1.70-0.80 (m, 14H)

[0021] Example 2. [Formula 33]

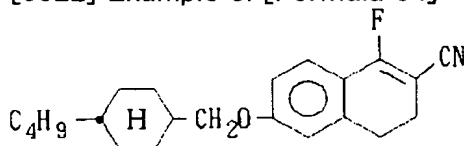


It compounded according to the example of manufacture (B). First, 6-methoxy-1-tetralone 25.0g (0.142 mols) was dissolved in 500ml of acetic acids, 80ml of hydrobromic acids was added 47%, and 1 evening heating reflux was carried out. Reaction mixture was condensed, the residue was opened in water, and the ether extracted. The ether layer was condensed, the residue was ***** from chloroform, and 6-hydroxy-1-tetralone (4)17.50g (76.1%) was obtained. 7.83g (0.045 mols) of diethyl azodicarboxylate was dropped dissolving and stirring 4.86g [of obtained phenol nature compounds] (0.03 mols), and trans-4-butyl cyclohexyl methanol 5.73g (0.033 mols), and triphenyl phosphine 11.79g (0.045 mols) to tetrahydrofuran 90ml, and it stirred at the room temperature for 3 hours. Reaction mixture is condensed, a silica gel chromatography (expansion solvent : ethyl acetate / hexane = 7/93) refines the residue, and it is 6. -(trans-4-butyl cyclohexyl)- Methoxy-1-tetralone 8.20g (87.0%) was obtained. 4.70g (63.0%) of specified substance was obtained from obtained tetralone 6.90g (0.022 mols) completely like the above-mentioned method [Synthesis, 449 (1981)].

¹H-NMR(200MHz,CDCl₃)

delta:8.00 (d, 1H), 6.85 (dd, 1H), 6.70 (brs, 1H), 3.85 (d, 2H) and 3.70 (dd, 1H), 3.20-2.90 (m, 2H), 2.60-2.30 (m, 2H), 2.00-0.80 (m, 19H)

[0022] Example 3. [Formula 34]



Dimethylamino sulfas trifluoride 1ml (7.4 millimole) was added to THF10ml cooled at -15 degrees C - -20 degrees C in ice-ethanol, and what dissolved 0.5g (1.48 millimole) of ketone compounds obtained by tetrahydrofuran 15ml from two drops of concentrated sulfuric acids and the example 2 was dropped. It stirred at 70 degrees C after the dropping end for 2 hours. It opened in water after the reaction end, sodium-hydrogencarbonate solution was added, ethyl acetate extracted, two silica gel chromatography refining (1st expansion solvent : chloroform, a 2nd expansion solvent : ethyl acetate / hexane = 5/95) of the residue was done after condensing an organic

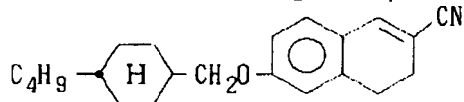
layer, and 0.24g (47.7%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta:7.42 (d, 1H), 6.81-6.74 (dd, 1H), 6.71 (brs, 1H), 3.76 (d, 2H) and 2.87 (t, 2H), 2.66-2.53 (m, 2H), 1.93-0.80 (m, 19H)

Elemental-analysis molecular formula (M. W.): C₂₂H₂₈NOF (341.46886)

Origin Base Theoretical value Actual measurement C. 77.38 77.23 H 8.26 8.25 N 4.10 4.27 F 5.56 5.59 O 4.69 - . [0023] Example 4. [Formula 35]

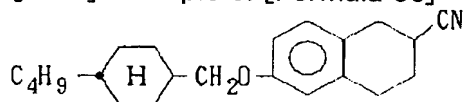


1.00g (2.95mmol) of ketone compounds obtained in the example 2 was dissolved in 2-propanol 40ml, 1.13g (30mmol) of bottom sodium borohydrides of ice-cooling was added, and it returned to the room temperature, and stirred for 3 hours. rare in reaction mixture -- it opened in HCl, the organic layer was condensed after extraction with ethyl acetate, silica gel chromatography (expansion solvent : chloroform) refining of the residue was carried out, and reduction alcoholic 1.10g was obtained The obtained alcohol was dissolved in toluene 50ml, 5g of potassium hydrogensulfates was added, and heating reflux was carried out at 120 degrees C for 3 hours. The inorganic substance was ****(ed), the silica gel chromatography (expansion solvent : chloroform) refined the residue after condensing a filtrate, and 0.87g (91.3%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

delta: -- 7.15 (s, 1H), 7.05 (d, 2H), 6.75-6.65 (m, 2H), 3.75 (d, 2H), 2.85 (t, 2H) and 2.50 (t, 2H), and 2.00-0.80 (m, 19H)

[0024] Example 5. [Formula 36]



0.48g (1.5mmol) of dihydronaphthalene derivatives obtained in the example 4 was dissolved in methanol 30ml, magnesium 2.2g (90mmol) was added under ice-cooling, and it stirred at the room temperature for 3 hours. The ether was added and extracted, after adding dilute hydrochloric acid to reaction mixture and dissolving magnesium. The ether layer was condensed, silica gel chromatography refining (expansion solvent : chloroform) of the residue was carried out, and 0.48g (98.5%) of specified substance was obtained.

¹H-NMR(200MHz,CDCl₃)

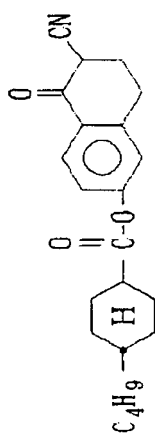
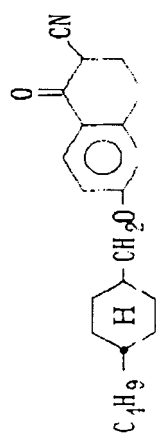
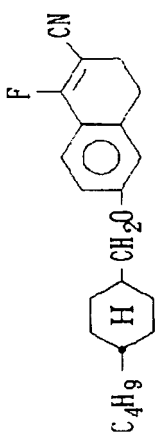
delta:6.95 (d, 1H) and 6.75- 6.55 (m, 2H), 3.70 (d, 2H), 3.15-2.70 (m, 4H), and 2.30-0.80 (m, 22H)

[0025] The phase transition temperature of the compound obtained in the physical-properties measurement above-mentioned example and the judgment of a phase were performed by using together the visual observation and the differential scanning calorimeter (DSC) by the polarization microscope. Moreover, about delta n and delta epsilon, it measured according to the reference method. The obtained result is shown in Table 1.

[0026]

[Table 1]

表 - 1

実施例	構造式	相転移温度 (°C)	Δn	$\Delta \epsilon$
1		$\begin{array}{c} 84.1 \quad 96.1 \\ \leftarrow \quad \quad \rightarrow \\ \text{K} \quad \text{N} \quad \text{I} \\ \quad \quad \quad 120.0 \end{array}$	0.045	-
2		$\begin{array}{c} 62.0 \\ \leftarrow \quad \quad \rightarrow \\ \text{K} \quad \text{S}_A \quad \text{I} \\ \quad \quad \quad 86.2 \end{array}$	-	-
3		$\begin{array}{c} 49.3 \quad 69.1 \\ \leftarrow \quad \quad \rightarrow \\ \text{K} \quad \text{N} \quad \text{I} \\ \quad \quad \quad 73.4 \end{array}$	0.12	14.6

[0027]

[Table 2]

表 - 1 (つづき)

4		$\begin{array}{c} \text{K} \rightleftharpoons \text{N} \xrightarrow{84.9} \text{I} \\ \text{58.8} \end{array}$	0.15	10.36 (30.5°C)
5		$\begin{array}{c} \text{K} \xrightarrow{56.5} \text{I} \\ \text{N} \xleftarrow{37.4} \end{array}$	0.072 (31°C)	3.31 (30°C)

(注) 液晶相などの各相は、次の記号で示した。

I : 等方相 ; N : ネマチック相 ; S_A : スメクチック A 相 ; K : 結晶相

[0028]

[Effect of the Invention] 2-alkyl-6-substitution which is the compound of this invention - 1, 2, 3, and 4-tetrahydronaphthalene derivative is a new compound, and in case it prepares the liquid crystal constituent used for a liquid crystal flat-panel display etc., it is one useful component. While the compound of this invention has high physical chemical stability and a stable nematic phase is shown, about a certain compound, it has the feature that a dielectric constant anisotropy ($\Delta\epsilon$) is large. Therefore, in case this compound is an additive effective in low-battery-izing of a liquid crystal constituent and builds a practical liquid crystal constituent about threshold voltage and a saturation voltage required for making a liquid crystal display element etc. drive, it is offered as one useful component. That is, compatibility with liquid crystal compounds, such as many of other liquid crystal compounds, for example, an ester system, an ether system, a carbonyl system, a biphenyl system, a phenylcyclohexane system, and a heterocycle system, is good, and it adds to the liquid crystal constituent containing these, and an

N-I point can be raised or it can improve other physical properties. Thus, in building the liquid crystal constituent used for a liquid crystal flat-panel display etc., this invention also offers the practical liquid crystal constituent containing at least one sort of these compounds while offering a compound useful as one component.

[Translation done.]